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British Association for the Advancement of Science

Reports on colloid chemistry and its general industrial application.

Vol.2.Second report. 1918.

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Department of Scientific and Industrial Research.

British Association for the Advancement of Science.

Reports on colloid chemistry

1918.

SECOND REPORT

ON

COLLOID CHEMISTRY

AND ITS

GENERAL AND INDUSTRIAL APPLICATION.

LONDON:
Printed and Published for the Department of Scientific and Industrial Research by His Majesty's Stationery Office.

1919.

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Department of Scientific and Industrial Research.

British Association for the Advancement of Science.

1918.

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PREFATORY NOTE.

THIS Second Report on Colloid Chemistry and its Industrial Applications is the outcome of the work during the year 1918 of a Committee under the Chemical Section of the British Association for the Advancement of Science. A Report for the year 1917 was prepared by the Committee and was subsequently published by the British Association under the title "First Report on Colloid Chemistry and its Industrial Applications." It is of great importance that each of these Reports on Colloid Chemistry shall be published immediately on completion, as otherwise much of its value will be lost.

Since the British Association, through financial difficulties consequent on the war, found itself unable to meet the greatly enhanced cost of publication for the Second Report the matter was laid before the Department of Scientific and Industrial Research. This Department considered that the results of the work should be made accessible on the grounds that they promise to be of considerable value to research workers in Colloid Chemistry, and to many branches of chemical industry. It was therefore arranged that this Second Report should be published by H.M. Stationery Office on behalf of the Department of Scientific and Industrial Research.

Department of Scientific and Industrial Research,

15, Great George Street,

Westminster, S.W.1.

21*st February*, 1919.

Colloid Chemistry and its General and Industrial Applications.—*Second Report of the Committee, consisting of* Professor F. G. Donnan (*Chairman*), Professor W. C. McC. Lewis (*Secretary*), Dr. E. F. Armstrong, Professor Adrian J. Brown, Dr. C. H. Desch. Mr. E. Hatschek, Professors H. R. Procter and W. Ramsden, Mr. A. S. Shorter, Dr. H. P. Stevens, *and* Mr. H. B. Stocks.

Introduction.

The plan already adopted of arranging the subject-matter under two heads, viz. (1), classification according to scientific subject, and (2), classification according to industrial process and general application of colloid chemistry to other sciences, has been employed in the preparation of the Second Report.

The subjects dealt with under the first head in the accompanying Report are:—

1. Peptisation and Precipitation.
2. Emulsions.
3. The Liesegang Phenomenon.
4. Electrical Endosmose, Part I.

The subjects dealt with under the second head are:—

1. Electrical Endosmose, Part II.
2. Colloid Chemistry in the Textile Industries.
3. Colloids in Agriculture.
4. Sewage Purification.
5. Dairy Chemistry.
6. Colloid Chemistry in Physiology.
7. Administration of Colloids in Disease.

The Committee has again to express its deep sense of obligation to the gentlemen who under somewhat difficult circumstances have compiled the various sections which make up the present Report.

It is hoped that the very valuable material which has now been collected in the First and Second Reports will serve the purpose of emphasising the fundamental importance of colloid chemistry for operations and processes which, at first sight, appear to be wholly distinct, and at the same time will serve to co-ordinate such information and to render it available for the benefit of all who are engaged in operations in which colloid chemistry plays a part.

A number of subjects have not as yet been considered. It is hoped that these will be discussed in the Third Report. In this connection the Secretary (*Muspratt Laboratory, University, Liverpool*) would be glad of suggestions from those engaged in chemical industry regarding subjects or problems met with in technical work which could be considered as coming within the scope of the Committee's activities. It is felt that such co-operation, which at the present time would be particularly valuable, is not impossible.

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REPORT ON PEPTISATION AND PRECIPITATION.

By Professor WILDER D. BANCROFT, *Cornell University.*

Sufficiently small particles will be kept in suspension in a liquid by the Brownian movements. Any method which will form small particles and will keep them from coalescing will give rise to colloidal solutions. Tentative theories of peptisation have been discussed by Lottermoser,[1] Jordis,[2] Mecklenburg,[3] and von Weimarn.[4] If we adopt Freundlich's view[5] that adsorption always lowers the surface tension, a theory of peptisation follows at once,[6] because an adsorbed film with a low surface tension on the solvent side and a high one on the other side will tend to disintegrate or peptise the other substance as internal phase.

When a liquid is adsorbed by a solid, it will tend to peptise it and in some cases will do so. Water peptises tannin readily and amyl acetate peptises pyroxylin. At higher temperatures the peptising action increases. Gelatine is peptised by warm and not by cold water. Glass is peptised by hot water[7] and vulcanised rubber by various heated organic liquids,[8] while fused baths peptise metals.[9]

There are a number of cases where mixed solvents will peptise a solid much better than either one alone—celluloid nitrate in ether and alcohol, caseine in pyridine and water,[10] and probably cinchonine in chloroform and alcohol,[11] as well as phloretine in ether and water.[12] The theory of this has not been worked out. Cellulose nitrate swells in alcohol and not in ether;[13] but it is not known whether this is universal or whether alcohol peptises cellulose nitrate at higher temperatures. Zein is also peptised in mixed solvents.[14]

Relatively little work has been done on direct peptisation by means of a dissolved non-electrolyte, but a good deal of stress has been laid on the cases where a non-electrolyte prevents the formation of a visible precipitate. A concentrated solution of sugar in water will prevent the precipitation of calcium silicate,[15] silver chromate, and silver chloride;[16] also of lime and of the hydrous oxides of copper,[17] uranium, and iron.[18] Invert sugar is about seven times as effective as cane sugar in holding up hydrous ferric oxide.

[1] Lottermoser, *Jour. prakt. Chem.* (2) **68**, 341 (1903); **72**, 39 (1903); **73**, 374 (1906); *Zeit. phys. Chem.* **62**, 371 (1908).
[2] Jordis, *Van Bemmelen Gedenkboek*, 215.
[3] *Zeit. anorg. Chem.* **74**, 260 (1912).
[4] *Lehre von den Zuständen der Materie*, **1**, 60 (1914).
[5] *Kapillarchemie*, **52**, 154 (1909); Patrick, *Zeit. phys. Chem.* **86**, 545 (1914).
[6] Bancroft, *Jour. phys. Chem.* **70**, 85 (1916).
[7] Barus, *Am. Jour. Sci.* (3) **41**, 110 (1891); (4) **6**, 270 (1898); **7**, 1 (1899); *Phil. Mag.* (5) **47**, 104, 461 (1899).
[8] Barus, *Am. Jour. Sci.* (3) **42**, 359 (1891).
[9] Lorenz, *Van Bemmelen Gedenkboek*, 395.
[10] Levites, *Zeit. Kolloidchemie*, **8**, 4 (1911).
[11] Oudemanns, *Jour. Chem. Soc.* **26**, 533 (1873).
[12] Schiff, *Zeit. phys. Chem.* **23**, 355 (1897).
[13] Private Communication from Professor Chamot.
[14] Galeotto and Giampalmo, *Zeit. Kolloidchemie*, **3**, 118 (1908).
[15] Weisberg, *Bull. Soc. Chem.* Paris (3), **15**, 1097 (1896).
[16] Lobry de Bruyn, *Ber. deutsch. Chem. Ges.* **35**, 3079 (1902).
[17] Graham, *Jour. Chem. Soc.* **15**, 253 (1862).
[18] Riffard, *Comptes rendus*, **77**, 1103 (1873).

Grimaux[19] showed that glycerine prevents the precipitation of hydrous ferric oxide by caustic potash.

If one ion of an electrolyte is adsorbed more than the other ion, it will tend to peptise the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the nature of the adsorbed ion. Univalent ions are not all adsorbed alike; nor are bivalent or trivalent ions. The order of adsorption is specific with each substance. Certain univalent ions are adsorbed by certain substances more than certain bivalent or trivalent ions.[20] In many cases there is, however, a marked tendency to increased adsorption with increasing valence, as formulated in Schulze's so-called law.[21] It seems to be a general rule that insoluble electrolytes adsorb their own ions markedly. Consequently, a soluble salt having an ion in common with a sparingly soluble electrolyte will tend to peptise the latter.

Freshly precipitated silver halides are peptised by dilute silver nitrate or the corresponding potassium halide,[22] the silver and the halide ions being adsorbed strongly. Many oxides are peptised by their chlorides or nitrates, forming so-called basic salts.[23] Sulphides are peptised by hydrogen sulphide.[24] Gelatine is liquefied or peptised by a potassium iodide solution. The peptisation of hydrous oxides by caustic alkali can be considered as a case of common ion or as the preferential adsorption of hydroxyl ion.[25] Hydrous chromic oxide gives an apparently clear green solution when treated with an excess of caustic potash; but the green oxide can be filtered out completely by means of a collodion filter, a colourless solution passing through.[26] Hantzsch[27] considers that hydrous beryllium oxide is peptised by caustic alkali, copper oxide is peptised by concentrated alkali,[28] and so is cobalt oxide.[29] In ammoniacal copper solutions part of the copper oxide is apparently colloidal and part is dissolved.[30] Freshly precipitated zinc hydroxide is peptised by alkali; but the solution is very instable, the zinc hydroxide often coagulating inside of half an hour.

The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate.[31] The bulk of the

[19] *Comptes rendus*, **98**, 1485, 1540 (1884).
[20] Bancroft, *Jour. Phys. Chem.* **19**, 363 (1915).
[21] Schulze, *Jour. prakt. Chem.* (2), **25**, 431 (1882); **27**, 320 (1884).
[22] Lottermoser, *Jour. prakt. Chem.* (2) **60**, 341 (1903); **72**, 39 (1905); **73**, 374 (1906) *Zeit. phys. Chem.* **62**, 371 (1908).
[23] Müller, *Ber. deutsch. chem. Ges.* **39**, 2856 (1906); *Zeit. anorg. Chem.* **52**, 316 (1907). Szilard, *Jour. Chim. phys.* **5**, 488, 636 (1907). Graham, *Jour. Chem. Soc.* **15**, 254 (1862).
[24] Spring, *Ber. deutsch. chem. Ges.* **16**, 1142 (1883). Prost, *Jour. Chem. Soc.* **54**, 653 (1888). Winssinger, *Bull. Soc. chim.* Paris (3) **49**, 452 (1888). Linder and Picton, *Jour. Chem. Soc.* **61**, 116 (1892). Meunier, *Comptes rendus*, **124**, 1151 (1897). Young, *Jour. Phys. Chem.* **21**, 1, 14 (1917).
[25] Bancroft, *Jour. Phys. Chem* **20**, 99 (1916).
[26] Fischer and Herz, *Zeit. anorg. Chem.* **31**, 352 (1902). Fischer, *Zeit. anorg. Chem.* **40**, 39 (1904). Nagel, *Jour. Phys. Chem.* **19**, 331, 569 (1915).
[27] *Zeit. anorg. Chem.* **30**, 289 (1902).
[28] Loew, *Zeit. anal. Chem.* **8**, 463 (1870). Fischer, *Zeit. anorg. Chem.* **40**, 39 (1904).
[29] Tubandt, *Zeit. anorg. Chem.* **45**, 368 (1905).
[30] Peligot, *Ann. Chim. Phys.* (3) **63**, 343 (1861). Guignet, *Comptes rendus*, **55**, 741 (1862). Grimaux, *Comptes rendus*, **98**, 1434 (1884).
[31] Hantzsch, *Zeit. anorg. Chem.* **30**, 289 (1902); **75**, 71 (1912); Fischer and Herz *Zeit. anorg. Chem.* **31**, 352 (1902); Klein, *Zeit. anorg. Chem.* **74**, 157 (1912).

evidence seems to be that alumina is not peptised appreciably by alkali and that it goes into solution as sodium aluminate,[32] though the other view has been supported.[33] Adsorption of hydroxyl ion accounts for the peptisation of silicic acid[34] and caseine by alkalies. Caseine can also be peptised by acids. A. Müller[35] has prepared colloidal solutions of aluminum, iron, cobalt, thorium, and yttrium oxides by peptisation with dilute hydrochloric acid, and Bentley and Rose[36] have peptised freshly precipitated alumina with 8 per cent. acetic acid. It is possible, but not probable, that the peptisation is done by a trace of metallic salt formed by the acid and not by the hydrogen ion.

There are no cases where it has been shown conclusively that peptisation is due chiefly to adsorption of undissociated salt, but undoubtedly such instances will be found. Water-peptisable colloids like gelatin,[37] gum arabic,[38] dextrine,[39] soap,[40] or saponine,[41] will peptise many precipitates, and they are often called protecting colloids, because they prevent the agglomeration and consequent settling of finely divided precipitates. Caseine is not peptised by water, but acts a protecting colloid when peptised by acids or alkalies; Hydrous chromic oxide when peptised by caustic potash can then prevent the precipitation of hydrous ferric oxide, &c. If too much ferric oxide is present, all the chromic oxide is carried down by it.[42]

Solutions of copper oxide in ammonia will peptise chromic oxide.[43] Molybdic acid is not precipitated from its salts by uranyl salts, but tungstic acid is. In presence of tungstic acid, practically all the molybdic acid is precipitated. This is obviously a case of adsorption and the converse is undoubtedly true that no tungstic acid would be precipitated in presence of a sufficient excess of a molybdate.[44] Aniline dyes, which are insoluble in benzene, can be peptised by a benzene-soluble colloid such as the so-called zinc or magnesium resinate.[45]

Since a colloidal solution is one in which a finely divided phase is kept from coalescing in some way, it is clear that there may be any number of colloidal aluminas, for instance, varying from anhydrous

[32] Herz, *Zeit. anorg. Chem.* **25**, 155 (1900). Hantzsch, *Zeit. anorg. Chem.* **30**, 289. (1902). Rubenbauer, *Zeit. anorg. Chem.* **30**, 331 (1902). Fischer & Herz, *Zeit. anorg. Chem.* **31**, 355 (1902). Slade, *Jour. Chem. Soc.* **93**, 421 (1908); *Zeit. anorg. Chem.* **77**, 457 (1912); *Trans. Faraday Soc.*, **10**, 150 (1914); Blum, *Jour. Am. Chem. Soc.* **35**, 1499 (1913).

[33] Mahin, Ingraham and Stewart, *Jour. Am. Chem. Soc.* **35**, 30 (1913).

[34] Graham, *Jour. Chem. Soc.* **17**, 324 (1864).

[35] Svedberg, *Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe.* 400 (1909).

[36] *Jour. Am. Chem. Soc.* **35**, 1490 (1913).

[37] Eder's *Handbuch der Photographie*, 5th Ed. 3, I, 28 (1902). Lüppo-Cramer, *Phot. Correspondenz*, **44**, 578 (1907).

[38] Lefort and Thibault, *Jour. Chem. Soc.* **42**, 1322 (1882).

[39] Lachaud, *Bull. Soc. Chim. Paris* (3) **15**, 1105 (1896).

[40] Spring, *Zeit. Kolloidchemie* **4**, 161 (1909); **6**, 11, 109, 164 (1910).

[41] Schiaparelli, *Jour. Chem. Soc.* **46**, 333 (1884).

[42] Northcote and Church, *Jour. Chem. Soc.* **6**, 54 (1854); Nagel, *Jour. Phys. Chem.* **19**, 331 (1915).

[43] Prud'homme, *Jour. Chem. Soc.* **25**, 672 (1872).

[44] Miss Hitchcock, *Jour. Am. Chem. Soc.* **17**, 480, 520 (1895); Wöhler, *Zeit. Elektrochemie*, **16**, 693 (1910).

[45] Soxhlet, *Art of Dyeing and Staining Marble, &c.* 76 (1902).

alumina (Al_2O_3) up to the most highly hydrous form that can be obtained. As a matter of fact, people have generally been satisfied with distinguishing only two sets of colloidal solutions, which they have called solutions of alumina and metalumina, stannic and metastannic acids, &c.[46] While adsorption will cause peptisation under suitable conditions, the disintegrating power of the adsorbed substance is relatively small and often is not sufficient to break up solid masses. A protecting colloid, for instance, will prevent the formation of a precipitate when it may not be able to disintegrate a massive precipitate.

The preparation of colloidal solutions by peptisation is usually classed under the general head of dispersion methods. Five different types may be distinguished:—

1. *Removal of Agglomerating Agent.*—If a precipitate has settled from a colloidal solution owing to the addition of too much of an agglomerating agent, the precipitate may go back into apparent solution if the excess of the agglomerating agent is washed out. No colloidal solution will be obtained if it is impossible to wash out the coagulating agent or if the agglomeration has gone too far.[47] If a silver halide precipitate is washed on a filter at once, the silver salt is apt to run through the filter when the excess of potassium salt has been removed and there is present only the amount which would have kept the silver halide in suspension originally. When the rare earth nitrates are precipitated by ammonia and then washed, they are liable to stay suspended in the liquid when the ammonium nitrate is nearly all removed. In alloy work stannic oxide should be washed with dilute nitric acid and not with water. Zinc sulphide is apt to form a colloidal solution when the ammonium salt is washed out,[48] and copper ferrocyanide does the same thing if all the copper sulphate is removed by washing.[49] In fact, Chautard[50] claims that the quickest way to wash a gelatinous precipitate is to evaporate the solution to dryness and heat before trying to wash. Merely evaporating on a water-bath is not always sufficient.[51]

2. *Addition of Peptising Agent.*—Instead of washing out a precipitating agent, a peptising agent may be added. Ammonia is very effective in suspending clay,[52] silicic acid is peptised readily by caustic soda,[53] and Prussian blue is peptised by oxalic acid or by potassium oxalate. In some cases the concentration of the peptising agent has to be high, as when oxides are peptised by alkali, and people usually assume the formation of compounds.

The action of soap on rouge or carbon black[54] looks like a disintegration; but it is not. If a suspension of carbon black in water

[46] Hantzsch, *Zeit. anorg. Chem.* **30**, 338 (1902); Bancroft, *Jour. Phys. Chem.* **19**, 232 (1915).
[47] Cf. Abegg and Schroeder, *Zeit. Kolloidchemie*, **2**, 85 (1907).
[48] Donnini, *Jour. Chem. Soc.* **66** II. 318 (1894).
[49] Berkeley and Hartley, *Phil. Trans.* **206** A, 486 (1906).
[50] *Jour. Chem. Soc.* **26**, 527 (1873).
[51] Wright, *Ibid.* **43**, 156 (1883); Kratz: *Jour. Phys. Chem.* **16**, 121 (1912).
[52] Skey, *Chem. News*, **17**, 164 (1868); **22**, 236 (1870); **34**, 142 (1876); see also Doelter, *Handbuch der Mineralchemie*, **2**, 122 (1912).
[53] Graham, *Jour. Chem. Soc.* **17**, 324 (1864).
[54] Spring, *Zeit. Kolloidchemie*, **4**, 161 (1909); **6**, 11, 109, 164 (1909). Bancroft, *Jour. Phys. Chem.* **20**, 107 (1916).

be filtered several times through filter-paper, the water will finally run through clear, and the carbon black will be held back by the filter-paper. If a soap solution be poured on the filter, a black filtrate is obtained and the filter-paper is no longer black. All the carbon black has passed through the filter-paper. The same thing can be done with rouge, except that a red filtrate is obtained instead of a black one. At first sight it seems that though the soap must have broken up the carbon or the rouge into finer particles, which then passed through the filter, but this is probably not so. The filter-paper is porous enough at first to let through the particles of carbon or rouge, as is shown by the fact that some of the suspended matter does pass through the filter at first. The cellulose adsorbs the carbon black or the rouge, and this clogs the filter to such an extent that the pores are not large enough to let the remaining particles through. The soap removes the rouge or the carbon black from the paper because it adsorbs these substances more strongly, and everything, therefore, goes through the paper. That this is the true explanation can be shown in two ways. In the first place, the experiment does not succeed if the rouge or the carbon is too coarse. In the second place, Spring showed that we are dealing with an adsorption of carbon black by filter-paper. If the black filter-paper be reversed and washed with water, the water removes only the black which is not in immediate contact with the paper.

3. *Mechanical Disintegration.*—If a solid be ground sufficiently fine it will necessarily form a colloidal solution for a time. This has been done experimentally by Wegelin[55] in the case of a number of metals. The addition of gelatin makes it easier to disintegrate ductile metals. Since a finely divided solid is more soluble, it is possible that it may go into solution and then precipitate in another form. This seems to happen with quartz. When reduced to an impalpable powder by long grinding, quartz can be converted into colloidal hydrous silicic acid merely by boiling with water.[56]

4. *Electrical Disintegration.*—When a direct current arc is formed under water between two wires, the metal is disintegrated and colloidal solutions of platinum, iridium, palladium, gold, silver, and cadmium may be obtained in this way.[57] Satisfactory conditions are obtained with 30 to 40 volts and 5 to 10 amperes. A trace of alkali in the water causes formation of finer particles, presumably owing to the stabilising effect of the hydroxyl ion. The disintegration is chiefly at the cathode.

The method is not satisfactory with organic liquids, because too much decomposition of the liquids takes place. Svedberg found empirically that this decomposition could be decreased very much if the current density were made as small as possible.[58] He therefore used an oscillatory discharge from an induction coil with a condenser in parallel or in series. The best results are obtained with large capacity, small self-induction, low resistance, and short

[55] *Zeit. Kolloidchemie*, **14** 65 (1914).
[56] Desch. *The Chemistry and Testing of Cement*, 58 (1911).
[57] Bredig. *Zeit. Elektrochemische*, **4**. 514 (1898); *Zeit. Phys. Chem.* **31**, 258 (1899).
[58] Svedberg, 424.

arc. By this improved method Svedberg succeeded in preparing colloidal solutions of all the metals, including the alkali metals. Liquid methane, ether and isobutyl alcohol at low temperature were especially satisfactory with the metals of the alkalies and the alkaline earths. The order of disintegration of some of the metals under similar conditions was found to be Fe, Cu, Ag, Al, Ca, Pt, Au, Zn, Sn, Cd, Sb, Tl, Bi, Pb, the iron being the least rapidly disintegrated and the lead the most rapidly disintegrated. There is no apparent relation either with the order of the boiling-points or with the order of disintegration by cathode rays or canal rays.

5. *Electrochemical Disintegration.*—With a lead cathode in caustic soda solution, the lead disintegrates when the current density exceeds a critical value, and the solution is coloured black like ink, with fine particles of metallic lead.[59] This is due to the temporary formation of a sodium-lead alloy, which then disintegrates in contact with water. Similar results can be obtained with cathodes of tin, bismuth, thallium, arsenic, antimony, and mercury. E. Müller[60] obtained colloidal solutions of tellurium with a tellurium cathode. This seems to be due to the formation of polytellurides, which break down and set free tellurium. In the presence of oxygen there may also be an oxidation of a telluride. Fischer[61] has obtained metallic copper in the solution by using a high current density with a copper anode in sulphuric acid. Cuprous sulphate is formed, which breaks down to metallic copper and cupric sulphate. This experiment has not yet been made to give colloidal copper; but this could probably be done if one were to add a suitable protecting colloid. The disintegration of all electrodes by an alternating current when the current density is high is undoubtedly due to the temporary formation and subsequent breaking down of a hydrogen or metallic alloy.

Three classes of colloidal solutions have been distinguished, in which the stabilisation is due: to adsorbed liquid: to adsorbed non-electrolyte, which may be in true solution or may be itself in colloidal solution; and to an adsorbed ion. The last case is the easiest one to treat theoretically and is therefore taken up first. So long as the particles are all charged positively or all charged negatively, they will repel each other and will not coalesce. If the charge is neutralised or counter-balanced in any way, the particles will agglomerate[62] unless some other factor comes in. If a suspension is stabilised by the preferential adsorption of hydrogen ion from hydrochloric acid solution, the solution contains free hydrogen ions, free chlorine ions, and the adsorbed hydrogen ions which make the suspension behave like a cation though with a different migration velocity from that of hydrogen. If the suspension is made to adsorb an anion in an amount equivalent to the hydrogen ion adsorbed, the

[59] Reed, *Jour. Franklin Inst.* **139**, 283 (1895).
Bredig and Haber, *Ber. deutsche. Chem. Ges.* **31**, 2741 (1898).
Haber and Sack, *Zeit. Elektrochemie* **8**, 245 (1902); *Zeit. Anorg. Chem.* **34**, 286 (1903).

[60] *Zeit. Elektrochemie* **11**, 521, 701 (1905).
Haber, *Ibid.* **11**, 660, 827 (1905).

[61] *Ibid.* **9**, 507 (1903).

[62] Hardy, *Zeit. Phys. Chem.*, **33**, 385 (1900). Burton, *Phil. Mag.* (6), **12**, 472 (1906); **17**, 583 (1909).

suspended particles will be electrically neutral. This can be done by adding an electrolyte with a readily adsorbed anion. Since this is a matter of selective adsorption, the concentration of the added anion necessary to cause an adsorption equivalent to the hydrogen adsorption will vary with each anion. To put the matter more generally, the amount of an electrolyte necessary to precipitate a colloidal solution will vary with the nature of the cation, the anion, and the dispersed phase. While it is generally true that an ion of higher valance will be adsorbed more strongly than one of lower valence, this co-called law of Schulze[63] is only a first approximation and should be considered only as a guide.

That some univalent ions are absorbed more strongly by some substances than some bivalent or trivalent ions is shown clearly in data by Odén on colloidal sulphur[64], given in Table I. In the second column are the liminal concentrations necessary to coagulate the sulphur, given in gram atoms per litre of the cations; in the third column are given the reciprocals of those values, the so-called atomic precipitating powers.

TABLE I.

Coagulation of Sulphur at 18°–20°.

Salt.	Liminal value gram-atoms. Cations per litre.	Atom c precipitating power of cation.
HCl	6	0·16
LiCl	0·913	1·1
NH_4Cl	0·435	2·3
$(NH_4)_2SO_4$	0·600	1·7
NH_4NO_3	0·506	2·0
NaCl	0·153	6·1
Na_2SO_4	0·176	5·7
$NaNO_3$	0·163	6·1
KCl	0·021	47·5
K_2SO_4	0·025	39·7
KNO_3	0·022	45·5
RbCl	0·016	63
CsCl	0·009	108
$MgSO_4$	0·0093	107·5
$Mg(NO_3)_2$	0·0080	125
$CaCl_2$	0·0041	245
$Ca(NO_3)_2$	0·0040	247
$Sr(NO_3)_2$	0·0025	385
$BaCl_2$	0·0021	475
$Ba(NO_3)_2$	0·0022	461
$ZnSO_4$	0·0756	13·2
$Cd(NO_3)_2$	0·0493	20·3
$AlCl_3$	0·0044	227
$CuSO_4$	0·0098	102
$Mn(NO_3)_2$	0·0096	105
$Ni(NO_3)_2$	0·0446	22·4
$UO_2(NO_3)_2$	0·0137	73

[63] *Jour. Prakt. Chem.* (2), **25**, 431 (1882); **27**, 320 (1884). Bancroft, *Jour. Phys. Chem.*, **19**, 364 (1915).

[64] *Der Kolloide Schwefel*, 156 (1912).

Under the conditions of Odén's experiments, sulphur is a negative colloid, and the precipitation is therefore due to an adsorption of cations. The first thing to be noticed is that hydrogen ion is not adsorbed strongly by sulphur, the precipitating power of hydrochloric acid being much less than that of lithium, ammonium, sodium, potassium, rubidium, or cæsium chloride. Instead of these univalent cations precipitating at the same concentration, the required concentration of lithium chloride is, in round numbers, one hundred times that of cæsium chloride. The luminal values for barium and strontium are nearly equal, but calcium chloride requires a distinctly higher concentration. If we take the different bivalent ions the values range from 0·0756 for zinc to 0·0022 for barium, a ratio of over thirty to one. The univalent cæsium ion has a greater precipitating power than the bivalent zinc, cadmium, nickel, and uranyl ions; and about the same precipitating power as the bivalent copper, manganese, and magnesium ions. The trivalent aluminum ion has about the same precipitating power as the bivalent calcium ion, and distinctly less precipitating power than bivalent strontium and barium ions. The specific nature of the adsorption comes out extraordinarily clearly with sulphur, about the only orthodox thing being that nitrate, chloride, and sulphate behave practically alike, though even here Odén considers that sulphate has a slight protecting action. This specific nature appears more clearly, perhaps, if we arrange the cations in order, the one with the greatest precipitating power coming first: Ba, Sr > Ca, Al > Mg, Cs, Mn, Cu > UO_2 > Rb > K > Ni, Cd, Zn > Na > NH_4 > Li > H.

Sulphur is admittedly an extreme case, but Freundlich[65] gives data for colloidal platinum from which I deduce the order: Al, Pb > Ba, UO_2 > Ag > K, Na. Bivalent lead has practically the same precipitating power as trivalent aluminum. Univalent silver is nearer to bivalent uranyl and barium than to univalent potassium and sodium. If more cations had been studied we should very likely have got more distinct evidence of specific action. As it is, it takes 130 millimols NaOH per litre to coagulate the platinum, and only 2·5 millimols NaCl. The change from chloride to hydroxide has a more marked effect than the change from sodium to barium. It seems very probable that barium hydroxide would have no greater precipitating power than sodium chloride. From Pappadà's experiments with colloidal silver[66] I deduce the following order of adsorption: Al > Ba, Sr, Ca > H > Cs > Rb > K > Na > Li. From these data Pappadà concludes that the migration velocity is the determining factor with the univalent cations; but this cannot be true. The difference between aluminum and hydrogen is not very great, one drop of M/10 HCl producing a coagulation and one drop M/20 $AlCl_3$. In tenth normal solutions potassium iodide, nitrate, and sulphate produce no coagulation. The reason given by

[65] *Kapillarchemie*, 352 (1909).
[66] Pappadà, *Gazz chim. ital.* **42**, I, 263 (1912).

the author is that these anions react with the colloidal silver. In normal solutions the iodides, nitrates and sulphates are said to precipitate at the same concentrations as the corresponding chlorides and bromides. The effect of concentration is a little obscure in other respects since 5 or 6 drops of normal KCl precipitate 2 cc. 0·06 per cent. Ag, whereas it takes only 30 drops N/10 KCl to produce precipitation. The essential thing, from my point of view, is that the different univalent cations have different liminal values, the difference between hydrogen and lithium is greater than that between hydrogen and aluminum.

From experiments on mastic[67] we get the data given in Table II.

TABLE II.

Coagulation of Mastic.

Salt.	Liminal value, gram atoms.	Atomic precipitating power of cation.
$NaCl$	1·0	1
$AgNO_3$	0·125	8
$HgNO_3$	0·00125	800
HCl	0·010	100
$CaCl_2$	0·025	40
$BaCl_2$	0·025	40
$ZnSO_4$	0·050	20
$Al_2(SO_3)_2$	0·0004	2,500
$Al_2(NO_3)_2$	0·0004	2,500
$FeCl_3$	0·0003	3,300

If we consider the mercury in mercurous nitrate as a univalent ion, it is very much out of place, precipitating at much lower concentrations than the barium, calcium, and zinc salts. Of course, the formula should be written $Hg_2(NO_3)_2$ with Hg_2 as a bivalent ion.[68] In this case the precipitating power becomes 1,600 instead of 800, which puts it up much nearer the trivalent cations than the bivalent ones. The order of cations is: Fe, Al > Hg_2 > H > Ba, Ca > Zn > Ag > Na. Only three anions are given in the table, so it is impossible to tell what effect the anions have. A good many experiments have been made on mastic with different acids, but the degree of electrolytic dissociation varies so as to make these results inconclusive. With Prussian blue Pappadà[69] found the order of the cations to be: Fe, Al, Cr > Ba, Cl > Sr, Ca > H > Cs > Rb > K > Na > Li. Sulphates, nitrates, chlorides, bromides, and iodides all behaved alike. Practically the same order of the cations was obtained for copper ferrocyanide.[70] In the cases studied by Pappadà the specific adsorption appears to play a very small part. The data for arsenic

[67] Freundlich, *Kapillarchemie*, 367 (1909).
[68] Ogg, *Zeit. phys. Chem.* **27**, 285 (1898).
[69] *Zeit. Kolloidchemie*, **6**, 83 (1911)
[70] Pappadà, *Zeit. Kolloidchemie*, **9**, 136 (1911).

sulphide,[71] however, give variety enough. The order of cations is Ce, In, benzidine, Al > new fuchsine, crystal violet > quinine > morphine, UO_2, Sr, Ca > Be, Zn, Ba > Ng > p-chloraniline, toluidine > aniline > strychnine > guanidine > H > K > Na > Li. The organic cations come in where they please and play havoc with any rule as to valency. The chlorides and nitrates give practically the same values, and the sulphates are not far out of line, though it seems probable that the restraining power of sulphate is rather greater than that of chloride or nitrate. The liminal values in gram atoms of the cation per litre are 0·0056, 0·0066, 0·0086, 0·110, and > 0·250 for potassium nitrate, sulphate, formate, acetate, and citrate, from which one can deduce that the order of adsorption of anion is : citrate > acetate > formate > sulphate > nitrate, chloride. It is a great pity that Freundlich did not try other combinations, such as barium acetate, for instance.

From the experiments on hydrous ferric oxide,[72] the order of adsorption of the precipitating anions appears to be Cr_2O_7 > SO_4 > OH > salicylate benzoate > formate > Cl > NO_3 > Br > I, while the order for the cations is : H > Ba > Mg > Tl, Na, K. The univalent ions do not all behave alike, and neither do the bivalent ones; but the upholders of Schulze's law can comfort themselves with the fact that the two sets do not overlap except in the case of hydrogen. There is no such comfort in the case of albumin. I have shown[73] that the probable order of adsorption of anions, so far as known, is : sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Here there is nothing even to suggest Schultze's law, and the firm belief which most people have in Schultze's law is probably one reason for the marked failure to account satisfactorily for the phenomena with albumin. With the cations albumin appears to be fairly orthodox, for the order of adsorption appears to be Th, UO_2 > Cu, Zn > Ca > Mg > Li > K, Na > NH though even here the lithium stands higher in the series than it has been found with other substances.

While there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions, and that the fundamental rule is that the adsorption is specific both as regards the adsorbing substance and the ion adsorbed.

Albumin is a specially interesting case because it is peptised readily by cations or anions. When it is negatively charged, as in a slightly alkaline solution, a strongly adsorbed anion will make it more negative and more stable. Consequently, precipitation by a sodium salt will be more effective the less readily the anion is adsorbed. On the other hand, in acid solutions the

[71] Freundlich, *Kapillarchemie*, 351 (1909). Freundlich and Schucht, *Zeit. phys. Chem.* **80**, 564 (1912).

[72] Freundlich, *Kapillarchemie*, 352, 358 (1909). Zsigmondy, *Kolloidchemie*, 187 1912). Pappadà, *Zeit. Kolloidchemie*, **9**, 233 (1911).

[73] Bancroft, *Jour. Phys. Chem.* **19**, 352 (1915).

sodium salt with the most strongly adsorbed anion will be the most effective in causing precipitation. Negatively charged albumin is precipitated readily by sodium chloride, and not at all by sodium iodide, while positively charged albumin is precipitated by sodium iodide much more readily than by sodium chloride.

If one over-runs the point of electrical neutrality, the suspension may become stable again because it is stabilised by preferential adsorption of an ion having the opposite sign. If one adds a little less than the equivalent amount of a dilute potassium bromide solution to a dilute silver nitrate solution, one gets a positively-charged colloidal solution of silver bromide because the silver bromide is stabilised by adsorbed silver ions. If one adds slightly more than the equivalent amount of the potassium bromide solution, there is obtained a negatively-charged colloidal solution of silver bromide, stabilised by adsorbed bromine ions. If more bromide solution is added, the silver bromide will coagulate because there will come a point at which the slight adsorption of the potassium ion counterbalances the adsorption of the bromine ion. In other words, silver bromide precipitates, when there is a distinct excess of silver nitrate, stays in suspension as a positively charged colloid when there is only a slight excess of silver nitrate, precipitates, when the suspension becomes electrically neutral, stays in suspension as a negatively charged colloid when there is a slight excess of potassium bromide, and precipitates when there is a distinct excess of potassium bromide. At the two ends of this series there is also the possibility of true solution of silver bromide in silver nitrate or potassium bromide.

An interesting case of the precipitation of a colloid by an electrolyte is to be found in the action of sea-water on muddy river water. Skey[74] pointed out that suspended mud is precipitated by electrolytes, and Waldie[75] has discussed the clearing of the water of the Hooghly. When a river flows into the ocean, the current becomes less, and some of the suspended mud is dropped on this account; but that is relatively unimportant in many cases. Schloesing[76] called attention to the fact that the formation of deltas is due primarily to the coagulation of the suspension by the electrolytes in the salt water. Another interesting case of the neutralisation of an electrical charge is the precipitation of positively charged colloids by β rays.[77]

Since the important thing in the neutralisation of an adsorbed ion is the adsorption of an ion of the opposite charge, we may get neutralisation when we have a colloid with the opposite charge. In other words, we may neutralise an adsorbed ion with another adsorbed ion instead of by a free ion. The usual statement is that sols having the same charge do not affect each other perceptibly, while sols having opposite charges precipitate

[74] *Chem. News*, **17**, 160 (1868).
[75] *Chem. News*, **30**, 37 (1874).
[76] *Jour. Chem. Soc.* **24**, 750 (1871).
[77] Hardy, *Jour. Physiology*, **29**, 29 (1903). Höber, *Physikalische Chemie der Zelle und Zewebe*, 332 (1911); Burton, *The Physical Properties of Colloidal Solutions*, 172 1916)

each other.[78] Neither of these statements is as accurate as it should be. I shall take up first the case of sols having opposite charges. Positive and negative colloids will precipitate each other when in proper proportions and provided adsorption takes place.[79] I see no theoretical reason why we should not have a positively charged and a negatively charged sol, neither of which adsorbed the other to any appreciable extent. In that case these two sols would not precipitate each other. Since complete neutralisation takes place only when one sol has adsorbed the amount of the sol carrying an equivalent amount of the ion having the opposite charge, it follows that the amount of one sol necessary to precipitate a given amount of another sol will vary with the degree of adsorption; it will therefore be a specific property and not an additive one. This can be tested experimentally on data by Biltz given in Table III.[80]

TABLE III.

1·4 mg. gold completely precipitated by					
CeO_2	Fe_2O_3	ThO_2	ZrO_2	Cr_2O_3	Al_2O_3
4	3	2·5	1·6	0·3	0·1 –0·2 mg.
28 mg. Sb_2O_3 completely precipitated by					
Fe_2O_3	ThO_3	CeO_2	ZrO_2	CrO_3	Al_2O_3
32	20	11	6·5	3·0	2·0 mg.
24 mg. Ag_2S_3 completely precipitated by					
Fe_2O_3	ThO_2	CeO_2	ZrO_2	Al_2O_3	Cr_2O_3
13	6	4	2	2	0·5 mg.

Alumina is more effective than chromic oxide in precipitating antimony sulphide, and much less effective in precipitating arsenic sulphide. The alumina must therefore be adsorbed more by antimony sulphide than chromic oxide, while the reverse must be true for arsenic sulphide. Cerium oxide is less effective than ferric oxide and thorium oxide in precipitating gold, but is more effective than either of these in precipitating the sulphides of antimony and arsenic. The phenomenon is thus specific, varying with the nature of the two colloids. This seems not to have been realised before. In fact, Freundlich says definitely[81] that ' one seems to find approximately the same order regardless of what sol is to be precipitated.' This statement is true, but it missed the important thing in the experiments, which was that the order was not always the same.

We can now take up the case of sols having the same charge. The statement that neither has any perceptible effect on the other is based solely on the fact that no precipitation occurs. We know, however, that cases of adsorption are not limited to colloids or electrolytes having opposite signs. Charcoal adsorbs both bases and acids. Silver bromide adsorbs silver ions or bromine

[78] Freundlich, *Kapillarchemie*, 444 (1909). Zsigmondy, *Kolloidchemie*, 56 (1912). Höber, *Physikalische Chemie der Zelle und Zewebe*, 294 (1914).
[79] Bancroft, *Jour. Phys. Chem.*, 18, 555 (1914).
[80] Freundlich, *Kapillarchemie*, 445 (1909).
[81] Freundlich, *Kapillarchemie*, 445 (1909).

ions, as the case may be. There is, therefore, no theoretical reason why precipitated hydrous ferric oxide might not adsorb chromic oxide, and *vice versa*. If the precipitated substance will do this, there is no reason why the peptised substance should not. Nagel[82] has shown recently that this does occur, and that it accounts for the behaviour of mixtures of chromic and ferric salts with excess of alkali. Hydrous chromic oxide is peptised by caustic potash, while hydrous ferric oxide is not. If the chromium salt is present in large amount relatively to the iron salt, the ferric oxide will adsorb the peptised chromic oxide and be peptised by it, going apparently into solution. If the ferric salt is present in excess, it will adsorb the peptised chromic oxide, carrying it out of the liquid phase. It is to be noticed that the chromic oxide, when in excess, acts as a so-called protecting colloid to the iron oxide. Everybody is familiar with the fact that gelatine is adsorbed by colloidal gold, for instance; but that is usually treated under the heading of protective colloids rather than under the heading of mutual action of two colloids. The case of chromic and ferric oxides is merely another illustration of the fact that the distinction between a suspension colloid and an emulsion colloid is now arbitrary and unsatisfactory.[83]

Coming back for a moment to the behaviour of two oppositely charged colloids, there is a special hypothetical case which is perhaps worth mentioning. Suppose we have two sets of finely divided particles, neither of which adsorbs the other appreciably, and let us also suppose that one set of particles adsorbs a given cation very strongly, while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well, but which will contain no free ions to speak of because, by definition, the cations have been practically completely adsorbed by one set of particles and the anions by the other set of particles. This particular case has not been realised, but an intermediate one seems to have been found by McBain and Martin[84] in sodium palmitate solutions.

'Most authors since Kahlenberg and Schreiner[85] have, as a matter of course, ascribed the conductivity exhibited by soap solutions largely to free alkali hydroxide. In previous papers from this laboratory the same tentative suggestion was made, but it was each time clearly stated that it was only a working hypothesis until these experimental data should be ascertained. Now it is certain that the conductivity of soap solutions is, only to a very minor extent, due to hydroxyl ions. Further, on account of the fact that the rise of boiling point in certain soap solutions is practically all required to account for the sodium ions alone,[86] the conductivity cannot be wholly ascribed to simple

[82] *Jour. Phys. Chem.* **19**, 331 (1915).
[83] Bancroft, *Jour. Phys. Chem.* **18**, 556 (1914).
[84] *Jour. Chem. Soc.* **105**, 965 (1914).
[85] *Zeit. Phys. Chem.* **27**, 552 (1898).
[86] McBain, *Trans. Faraday Soc.* **9**, 99; *Zeit. Kolloidchemie*, **12**, 256 (1913).

palmitate ions. The suggestion we made is that we have here a new type of aggregate or micelle, the mobility of which, owing to the reasons given in the paper cited, is comparable with that of a true anion. Of course, further investigations are proceeding in this laboratory in order to bring this to the test of direct experiment. Incidentally, the above shows, further, that undissociated soap is present chiefly or entirely in colloidal form.'

As I see the matter, the sodium palmitate is hydrolysed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate, and possibly by the insoluble palmitate acid also, though this seems less probable. The adsorbing substance thus becomes the anion, owing to the adsorbed hydroxyl. Because of electrometric measurements, McBain [87] considers that there is practically no hydrolysis. Electrometric measurements only show the concentration of hydroxyl ions in solution. I do not believe for a moment that an adsorbed hydrogen ion or hydroxyl ion behaves electrometrically like a free hydrogen or hydroxyl ion. An adsorbed chlorine ion, for instance, would not give a test with silver nitrate. Under these circumstances the electrometric measurements are satisfactory for showing the concentration of hydroxyl ions in the solution, but they are utterly worthless for showing the degree of hydrolysis of sodium palmitate. For the same reason I am very sceptical as to any conclusion in regard to albumin solutions which is based on electrometric measurements[88]

So-called irregular series[89] have been observed when a suspension of a positively-charged colloid is added to a suspension of a negatively-charged colloid. When increasing concentrations of aluminium sulphate were added to a negatively-charged solution of mastic there was at first no precipitation, and the suspension was charged positively because the mastic was present in excess. At higher concentrations of aluminium sulphate, the suspension became electrically neutral, and complete precipitation took place. At still higher concentrations the mastic was held in suspension by the hydrolysed alumina, and the suspension was charged positively. At still higher concentrations of aluminum sulphate complete precipitation occurred. This apparently abnormal result is due to the fact that the experiment is not exactly what it purports to be—the addition of one colloidal solution to another. Instead of adding a colloidal solution of alumina, there was added a so-called solution of aluminum sulphate, which hydrolysed to colloidal alumina and sulphuric acid, with possibly some aluminum sulphate left unchanged especially in the higher concentrations. The amount of free sulphuric acid is always equivalent to the amount of alumina, and the two concentrations increase proportionally. The so-called abnormal precipitation at the higher concentrations is merely a precipitation by sulphate ions, and is absolutely normal.

[87] McBain and Martin, *Jour. Chem. Soc.* **105**, 957 (1914).
[88] Bancroft, *Jour. Phys. Chem.* **19**, 349 (1915).
[89] Neisser and Friedmann, *Zeit. angew. Chem.* **1906**, 1953; Bechhold, *Zeit. Phys. Chem.* **48**, 285 (1904); Buxton and Teague, *Zeit. Phys. Chem.* **57**, 47, 64 (1907); Freundlich, *Kapillarchemie*, 402 (1909).

Since the precipitation of one colloid by another may take place within a relatively narrow range of concentrations, it is not surprising that people have postulated the existence of definite chemical compounds in order to account for the precipitates. The literature on the subject is in a worse state even than that on the so-called basic salts. For instance, ferric arsenate, aluminum silicate, stannic phosphate, and cupric eosinate are not formed under ordinary conditions by precipitation from solutions. The precipitation is due to the mutual coagulation of two colloids, though the resulting precipitate may simulate a compound to the extent that it may be peptised without change under certain conditions.

While the theory of peptisation and precipitation, as outlined, accounts satisfactorily for most of the facts, there are certain points which are not covered by it at present. A mixture of the two water-peptisable colloids, gelatine and gum arabic, is said to behave exactly like casein.[90] Under certain conditions gelatine and tannin form an insoluble or non-peptisable mixture;[91] but we do not know why. The case of chrome tanning is not difficult because the chromic oxide would not normally be peptised under the conditions of the experiment, and it has been shown that there is no necessary change in the gelatine.[92] We also cannot account at present for the stability or instability of metal sols in different organic liquids; in this case as well as in the other two, the trouble is in our ignorance of the facts and not in any shortcomings of the theory.

EMULSIONS.

By E. Hatschek, *Sir John Cass Technical Institute, London.*

The term Emulsion is used in the following to denote a disperse system, both phases of which, *considered in bulk and at ordinary temperature*, are liquid. The qualifying clause, although not generally stated in such explicit terms, seems desirable as, on one hand, the distinction between liquid and solid becomes somewhat vague with particles approaching ultra-microscopic dimensions, while, on the other, the same system, *e.g.*, rosin in water, may be a suspension at lower and an emulsion at higher temperature.

One characteristic of emulsions, which distinguishes them sharply from systems with solid disperse phase, follows immediately from the definition: there is no upper limit to the ratio: Volume of disperse phase/Volume of continuous phase. With solid or, better, undeformable particles of disperse phase there is such a limit (apart from the ideal case of space-filling polyhedra of equal size) which, for spherical particles of uniform radius, is approximately 74/26.

It is obvious that, with a liquid or deformable disperse phase, spherical particles in closest contact do not constitute a limiting case,

[90] Tiebackx, *Zeit. Kolloidchemie*, **8**, 198, 238 (1911).
[91] Wood, *Jour. Soc. Chem. Ind*, **27**, 384 (1908).
Von Schroeder, *Zur Kenntniss des Gerbeprozesses.*
Levites, *Zeit. Kolloidchemie*, **8**, 4 (1911).
[92] Lumière and Seyewetz, *Bull. Soc. Chim.*, Paris (3) **29**, 1077 (1903).

as—at least theoretically—a further increase in the relative volume of disperse phase can lead to flattening at the points of contact of contiguous spheres and eventually to a polyhedral structure of the system. A limit is only reached when the thin films of continuous phase which separate the polyhedra of disperse phase are no longer capable of cohering. The practical possibility of such systems is demonstrated by some of S. U. Pickering's emulsions with up to 99 per cent. of disperse phase. The complete conditions for the stability of such films will be discussed further on, but it can be said at once that a low inter-facial tension is, if possibly not sufficient, certainly necessary.

Conversely, emulsions with a very low content of disperse phase, in which the particles are small and separated by layers of continuous phase of some thickness compared with the extent of interface, are possible and moderately stable even when the interfacial tension is high, viz., of the order of 30 to 40 dyne/cm. Such emulsions may be produced by agitation, by distilling the two phases together, or by 'precipitating' an alcohol or acetone solution of the disperse phase with a large excess of water. The properties of such emulsions with a disperse phase consisting of mineral oils, aniline, nitrobenzene, oleic acid or castor oil, amounting to one part in a thousand, or less, of the total volume, are throughout those of fine suspensions or of suspensoids. The (negative) electric charge is of the same order as on suspensoid particles (Lewis); is similarly affected by hydrogen and hydroxyl ions (Ellis); the maximum concentrations at which the emulsions are stable are of the same order as for suspensoid sols (Lewis), and the phases may be separated by filtration through suitable septa under considerable pressure (Hatschek). The effect of interfacial tension is altogether subordinate to that of the electric factors.

Emulsions containing larger percentages of disperse phase than those mentioned, in particles of microscopic or approaching microscopic size, are stable, or in fact anything more than transient, only when the interfacial tension between the phases is low, as has already been mentioned. In the emulsions occurring in nature, such as milk or latex, this is generally brought about by the protein content of the continuous phase, while in the emulsions prepared artificially the agent which lowers the interfacial tension is very generally a soap. The stability of such emulsions is, however, again dependent on the phase ratio and is generally not complete unless this approaches the figure corresponding to closest packing. Thus, if oil and a dilute soap solution are shaken until the whole of the oil is dispersed, the resulting emulsion separates into a layer of soap solution containing only a very small fraction of oil and a 'cream' containing 75 per cent., or more, of oil; the latter is stable, provided the walls of the containing vessel are wetted only by the continuous phase and no oil in bulk is in contact with the cream. The rate of separation depends naturally on the difference in density of the phases, the viscosity of the continuous phase and the degree of dispersion: it is obvious, although the case has chiefly a theoretical interest, that a system stable in all ratios is conceivable if both phases have the same density, *e.g.*, castor oil in water with a little alcohol.

The connection between low interfacial tension and emulsification was first insisted on by Quincke, but the principal quantitative investigations are due to Donnan. They comprise experiments carried out with the drop pipette on the emulsification of glycerides in alkali solution, which show, in agreement with Quincke, that free fatty acid, *i.e.* the possibility of soap formation at the interface, is a necessary condition if emulsification is to take place; determinations of the drop numbers for hydrocarbon oils discharged into solutions of salt of the fatty acids, and experiments in which the hydrocarbon oil was dispersed in these solutions by shaking under strictly defined conditions. The two last series give concordant results and show that the first salt of the fatty acid series to exert an appreciable emulsifying action is the one which shows the first marked reduction of surface tension, viz. that of lauric acid. Donnan also finds that there is an optimum concentration of soap, and explains it as due to the balance between the reduction of interfacial tension, which promotes, and the electrolyte effect, which counteracts, dispersion.

A similar result, viz. that increase of soap concentration beyond a certain limit was detrimental to emulsification, had been obtained by S. U. Pickering. According to him the optimum concentration depends both on the phase ratio and on the absolute volumes of the phases, so that no simple explanation appears to offer itself. The same author also gives a number of experiments in which the emulsifying agent is not in solution—either true or colloidal—but a precipitate such as ' basic iron, copper or nickel sulphate,' *i.e.* the precipitates formed by adding lime water to the respective sulphates. If water containing one of these substances is agitated with oil—more particularly mineral hydrocarbons of 250° to 359° boiling-point and about 0·85 sp. gr.—the oil is completely emulsified. After an examination of various finely divided solids which show only a transient effect or none at all, Pickering comes to the conclusion that the chief factor in the formation of stable emulsions of oil as disperse phase in water is the existence of a layer of small solid, non-crystalline particles which *are more easily wetted by water than by oil* (the italics are mine, E. H.) at the interface.

While Pickering thus concludes that a low interfacial tension is not the principal, or in fact a necessary, condition of emulsification, the discrepancy between the two views is probably only apparent, at any rate if the ' solid ' state of the particles in the interfacial layer is not insisted upon. If low tension is not the direct agent it is nevertheless active indirectly in bringing about—in such solutions as alone come into question—the formation of adsorption films having some of the properties postulated. On the other hand, the substances used by Pickering would obviously not accumulate at the interface (more strictly on the water side of it) unless this arrangement led to a lowering of the interfacial tension.

That a film or membrane covering the whole of the interface is a necessary condition of stability in emulsions is the conclusion pronounced by W. D. Bancroft after a most exhaustive review of the available material. The relative solubility of this film in the two phases, or the difference in interfacial tensions between them and the film, determines the nature of the emulsion, *i.e.* which of the

two phases, in given conditions, will be the disperse and which the continuous phase.

These views derive strong confirmation from a series of experiments by G. H. A. Clowes. He prepares an emulsion with oil as disperse phase by shaking olive oil with a dilute solution of NaOH in water. If a quantity of $CaCl_2$ slightly in excess of the equivalent of the NaOH is added to this emulsion, it transforms itself spontaneously into one having water as disperse and oil as continuous phase. This can be re-converted into the original emulsion by adding NaOH until the original OH^1 concentration is restored. Magnesium, iron, and aluminium have an effect similar to that of calcium. Since the oleates of these metals are much more soluble in oil than in water, their formation would cause a considerable reduction in the interfacial tension between the film and the oil phase, so that the film would tend to become convex towards the oil and concave towards the aqueous phase, *i.e.*, oil would become the continuous phase and water the disperse. The whole process is an actual reversal and is therefore sharply distinguished from such phenomena as the separation of emulsions into two (no longer disperse) phase by the addition of electrolytes or of substances which decompose the material of the interfacial film.

Evidence similar, and complementary, to that afforded by Clowes's experiments is provided by an investigation by A. U. M. Schlaepfer, the object of which was to produce emulsions of water dispersed in oil by using a finely divided substance more completely wetted by oil than by water: soot accomplished the desired result.

Earlier experiments by Walter Ostwald, made with the intention of determining the type of emulsion which would result from the agitation of oil with water only, showed that either type was possible and that the result depended largely upon secondary factors, such as the state of the containing vessel and its previous wetting by one or the other phase. Conclusions drawn by this author regarding the limiting phase ratio have been proved incorrect both theoretically and experimentally. Donnan also found that the state of the vessel introduced considerable experimental complications. Although the method used by these and other authors—viz., agitation of the total volumes of both phases—is perhaps as good as any other arbitrary method, it neither corresponds to the probable process of formation of natural emulsions, nor to the technical methods adopted for the production of stable emulsions, in which the gradual addition of the disperse phase during, and *pari passu* with, the process of dispersion is generally considered an essential condition of success.

The theoretical interest of emulsions is considerable and is likely to become even greater. Viewed as disperse systems of two liquid phases they are the only ones in which the phase ratio is accurately known and therefore specially adapted for studying the physical properties, *e.g.*, the viscosity of such systems. They have also acquired very great importance in biology in view of some modern hypotheses on the constitution of protoplasm, the possible existence of lipoid films and cognate phenomena, such as the action of 'antagonistic' ions and of anæsthetics. While at present the conclusions respecting such complicated problems drawn from the study

of comparatively simple and coarse systems may perhaps constitute a theoretical edifice somewhat disproportionately large for its slight experimental foundation, there can be no doubt that the trend of research is in the right direction.

Technically also emulsions are of considerable importance. They are employed—speaking, of course, very generally—where it is necessary to administer or exhibit a liquid in a varying degree of dilution, while the ordinary solvents for it are inadmissible on economical, technical, or physiological grounds In such cases, or in a great number of them, the active liquid may be used as disperse phase of an emulsion, the continuous phase of which is so selected as to be indifferent; in addition it must wet, or be absorbed by, the surfaces to which the emulsion is eventually applied. Examples are: the medicinal emulsions of such liquids as cod-liver oil or petroleum (in which further desirable ingredients like malt extract, hypophosphites, &c., may be in solution in the aqueous phase); emulsions of cresols and other substances for use as antiseptic and anti-parasitic preparations; fat solvents such as carbon tetrachloride emulsified with 'monopol' soap (obtained by saponifying sulphenated castor oil); emulsions of fats in a great variety of menstrua and used as leather 'foods' and dressings, &c. The preparation of such emulsions is, of course, generally a trade secret; as regards the emulsifying agent, this is, however, very generally a soap in all technically used emulsions.

Emulsions occur in industrial processes as undesirable by-products, such as very persistent emulsions of mineral oils or of wool-fat in the course of refining; the condense water from reciprocating engines, which contains the oil used in the lubrication of slide valves and cylinders and is a very perfect type of the stable oil-water emulsion, &c. 'In all these cases the means of preventing the formation of an emulsion, or of separating it when formed, can be deduced from the theoretical consideration set forth above, although unfortunately their practical application is in many cases somewhat difficult.

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G. A. H. CLOWES, On reversible emulsions and the *rôle* played by electrolytes in determining the equilibriums of aqueous oil systems, 'Proc. Soc. for Exp. Biol. and Med.'; **11**. 1, 1913.

G. A. H. CLOWES, The action of electrolytes in the formation and inversion o oil-water systems, with some biological applications.

This paper, like the preceding one, describes experiments with emulsions obtained by dispersing olive oil in dilute NaOH solution. By adding $CaCl_2$ in excess of the alkali they are spontaneously transformed into emulsions having water as disperse phase, which can be re-transformed into the first type by adding NaOH in excess.

M. H. FISCHER and M. O. HOOKER, On the formation and decay of emulsions, 'Koll.-Zeitschr.'; **18**, 129, 1916.

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The author, following Pickering, concludes that a finely divided solid more easily wetted by oil than by water should be capable of producing emulsions with water as disperse phase and proves his conclusion experimentally by using soot as emulsifying agent.

THE LIESEGANG PHENOMENON.

By E. HATSCHEK, *Sir John Cass Technical Institute, London.*

This phenomenon was observed by its discoverer, after whom it is called, when carrying out the following experiment in the course of some researches on Golgi's method of staining animal tissues with silver chromate:

A glass plate is coated with 5 per cent. gelatin gel containing a small amount of potassium bichromate. A drop of strong silver nitrate solution is then placed on the gel and immediately begins to diffuse into the latter. The silver nitrate of course reacts with the bichromate in the gel, the products of reaction being silver bichromate and potassium nitrate. Although there is thus a continuous supply of both components, the insoluble silver salt is, however, not deposited in a continuous zone round the periphery of the original drop, *but in a series of concentric rings, separated by apparently clear zones*, the width of which increases with the distance from the centre.

The importance of the phenomenon was immediately perceived by R. E. Liesegang, who made it the subject of a very large number of experiments of great ingenuity, and who first suggested that it supplied the simplest explanation of the formation of a natural product, viz., of banded agates. It may be as well to

anticipate somewhat and to indicate at once the reasons for attaching importance to what at first sight may appear only a curious laboratory experiment. A large number of stratified structures occur both in organic and inorganic nature, the explanation of which has so far generally involved one or more of the following assumptions: a periodic supply of either or both components of a reaction; a periodic supply of a catalyst, activating or inhibiting agent; or, finally, a periodic external agency, such as, *e.g.*, variations of mean temperature. The Liesegang phenomenon, on the other hand, is proof that periodic structures may appear where all factors which can possibly exert any influence are constant. Where it is applicable as the basis of explanation it therefore leads to that economy of assumptions which is the desideratum of every hypothesis.

The conditions of the experiment have been varied by Liesegang and subsequent observers. The gel containing one component may be allowed to set in a test tube and the solution of the other poured on top. Or the gel may fill the bend of a U-tube and two solutions may diffuse into it in opposite directions from the limbs. Finally, bodies of gel containing one component may be submerged in solutions of the other. The results are substantially the same in all cases, although a given reaction may not produce them in an equally marked manner with every arrangement.

The phenomenon has also been studied in gels other than gelatin such as agar and silicic acid, and even in porous media of very much coarser structure than gels. The nature of the gel, and to a much slighter degree its concentration, are now fully proved to have a marked specific influence on the result with any given reaction. Thus, the reaction between silver nitrate and potassium bichromate leads to stratifications in gelatin, but not in agar, while on the other hand the reaction between lead nitrate and potassium chromate produces them in agar, but not in gelatin, while neither of the two leads to a stratified deposit if it takes place in silicic acid gel. A great number of reactions have also been investigated, some in all three gels and over wide ranges of concentrations, and well-marked stratifications have been obtained particularly with the following precipitates: lead iodide and lead chromate in agar, lead carbonate in agar and in silicic acid, phosphates of the heavy metals in various gels, sulphides, in various gels and in sand, &c.

Certain reactions, within wide limits of concentration, do not produce stratifications in certain gels. It has, however, been shown by Liesegang and by Hatschek—and the point is again of importance for the explanation of natural structures—that they can nevertheless be obtained as pseudo-morphoses after an intermediate product of reaction. Thus Liesegang places a drop of silver nitrate solution on a gelatin film containing sodium chloride; the resulting silver chloride forms only a continuous band. If a small fragment of potassium bichromate is placed some distance from the edge of the drop of silver nitrate, the usual silver chromate strata are formed round it when the silver salt has diffused so far, but are promptly transformed into silver chloride. The final result is stratifications of silver chloride round the site of the bichromate, although such

cannot be produced directly. By a slightly different procedure Hatschek obtains strata of lead chromate in gelatin, also as pseudomorphoses after silver chromate, although the reaction between lead nitrate and potassium chromate in gelatin leads only to a continuous band of lead chromate in the ordinary way.

Microscopic observation of the stratifications, both while in course of formation and after completion of the reactions, have been made by Liesegang himself and by later investigators. Only in a few reactions—of which the original silver chromate one is the best example—are the ' clear ' spaces between the rings practically free from the insoluble compound: in most cases the rings contain a large number of small, and the clear spaces a small number of large, crystals or crystalline aggregates. A striking microscopic illustration is afforded by cadmium sulphide in silicic acid gel, which exhibits no clear spaces at all, but a continuous succession of alternately yellow and pink bands. As is well known, the two shades are due to the difference in the size of the particles and both may be obtained by precipitating aqueous solutions of different concentrations. It is an open question whether, in many cases, the actual amount of reaction product in equal volumes of ring and clear space is not approximately the same.

As regards the theory of the phenomenon, the first explanation of the origin of periodic deposits was given by Wilhelm Ostwald. It is based on the assumption of ' metastable ' supersaturation, and is, in fact, the principal experimental evidence adduced by him for the existence of solutions in that condition. According to him; silver chromate is formed as the silver nitrate diffuses into the bichromate-gelatin, but at first remains in supersaturated solution until the limit of metastability is reached. When this happens, the silver chromate is precipitated and ' on the precipitate thus formed the silver chromate, *in respect of which the vicinity of the ring is supersaturated* (the italics are mine, E. H.) is deposited and reinforces it; this continues until the soluble chromate removed from the vicinity has gone into the precipitate.'

H. Bechhold, while generally accepting this theory, has shown that it is at least incomplete by demonstrating conclusively that the phenomenon is profoundly affected by factors which it fails to take into account, such as the solubility of the precipitate in the second reaction product, *e.g.*, the solubility of silver chromate in ammonium nitrate, ammonium bichromate having been employed in his experiments.

R. E. Liesegang also realised that the *experimentum crucis* would be the failure to produce a second ring system in a layer of gelatin already containing one, since the crystals forming the latter should obviously prevent supersaturation anywhere in their vicinity. He nevertheless succeeded in obtaining such a secondary system, but found that it was formed at a level below that of the primary stratifications. This result satisfied him that the experiment did not refute the supersaturation theory, a conclusion which it is difficult to accept. There is no obvious reason why a deposit of silver chromate which *ex hypothesi* (see the italicised passage in the quotation from Ostwald) prevents supersaturation radially over some distance

amounting to millimetres, should not do so equally at right angles to that direction, viz., into the depth of the layer of gelatin.

E. Hatschek carried out experiments of a more direct character in the test tube. Crystalline lead iodide was suspended in agar containing also potassium iodide. When lead nitrate solution was allowed, to diffuse into this gel, the usual, very perfect stratifications of lead iodide were formed, although crystalline nuclei were disseminated through the gel and should have made supersaturation impossible.

R. E. Liesegang does not consider that this result is incompatible with the supersaturation theory and suggests that the ' radius of action ' of the nuclei is too small to prevent the formation of strata which, with the particular reaction, occur at very small distances from each other. Without going into any speculations regarding the mechanism of this action, it can be said *a priori* that Liesegang's objection, if valid, would be equally fatal to Ostwald's theory itself.

The reason suggested by Liesegang to prove his own experiment inconclusive is, finally, eliminated in a somewhat similar experiment by L. J. de Whalley (published by E. Hatschek). He obtained a second system of stratifications of lead chromate in agar, which already contained a very fine system of strata of the same compound, *in a test tube*. As the reacting solutions in this arrangement must inevitably pass through, and meet in the vicinity of, existing strata, the case is different from that of the flat layer used by Liesegang, and appears to leave no escape from the conclusion that supersaturation was prevented throughout the formation of the second system of strata.

An alternative theory of periodic precipitation has been advanced by S. C. Bradford and supported by some experimental evidence, the most striking of which consists of photographs of preparations in strongly coloured solutions, such as the alkali chromates. According to him, one of the reacting solutes is adsorbed by the layer of precipitate, the result being a zone practically free from it, so that the clear space between the strata is at once accounted for. Considering the uncertain and conflicting results of adsorption experiments with solutions of electrolytes, it would be desirable to support what is undoubtedly an attractive suggestion by direct evidence—which Bradford so far has not obtained—that the solutes in question are actually adsorbed by the appropriate precipitates, *e.g.*, that potassium chromate is really adsorbed by lead chromate, or potassium sulphides by lead sulphide.

Apart from the difficulties already set forth, any theory must be pronounced inadequate which leaves—as do both Ostwald's and Bradford's—the gel out of account altogether. There is an abundance of material to show that the same reaction, if carried out in different gels, leads to entirely different results, in other words, that the gel has a specific effect and does not merely act as an indifferent medium which prevents mixing or currents. In this connection a suggestion made by H. Freundlich incidentally in a paper on another subject is of interest: that the formation of periodic strata may be an instance of the coagulation by electrolytes of a suspensoid

sol. While at first sight the distinction between a sol of, say, silver chromate and a ' metastable supersaturated solution ' of the same substance may (apart from the fact that we know hardly anything definite about the latter type of systems) seem rather subtle, further consideration shows that the former assumption immediately explains the specific effect of the gel. If electrolyte coagulation is the deciding factor, the protective effect of the gel must play an important part in promoting or inhibiting the formation of strata, and some such effect is easily traced in the comparative material collected principally by E. Hatschek. The consistent differences in the results obtained in gelatin, agar, and silicic acid gels point in this direction, as the protective effects of the three substances are widely different: taking Zsigmondy's ' gold figures ' as measuring this property, the protective effect of gelatin and agar is respectively 100 and 2, while that of silicic acid is negligible. These facts, of course, form merely the starting-point for a theory of the Liesegang phenomenon, and a very large amount of work would still be required to show its general validity.

The lack of a general theory of the formation of the Liesegang stratifications does not, of course, preclude suggesting a similar origin of stratified structures in nature or attempts to reproduce such experimentally. Liesegang led the way by explaining the bands in agate in this fashion, *i.e.*, by diffusion of iron salts into the gelatinous silica from which the stone probably originates, in preference to the earlier assumption of alternate deposition. Many similar suggestions in regard to both geological and histological examples are thrown out in his book entitled ' Geological Diffusions ' and in his numerous papers. The importance of the phenomenon for botanical anatomy and histology has been insisted on chiefly by E. Kuester. Its possible bearing on the transformation of cartilage into bone has been pointed out by H. Bechhold, and experimental work on this subject should be very fruitful. E. Hatschek and A. Simon have shown that a whole series of apparently disconnected peculiarities of gold deposits in quartz can be explained by assuming the latter to have originally been gelatinous silicic acid, in which the reduction of the solutions of gold salts was brought about by one of many possible agents.

In all these directions little more than a beginning has been made, and the experimental reproduction and elucidation of natural periodic structures should for a long time to come be one of the most fruitful fields for applied colloidal chemistry. It seems probable that investigation will have to be extended to gels made anisotropic by stress, since it is evident that most of the gel-like constituents of organisms are in such a condition, at least during long periods.

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ELECTRICAL ENDOSMOSE. I.

By T. R. Briggs, *Cornell University*.

1. *Electrical Endosmose Cataphoresis and Allied Phenomena.*

On passing an electric current through a porous diaphragm immersed in a liquid, one often observes a flowing of the liquid through the diaphragm; this flow is commonly from the anode to cathode, but may take place in the opposite direction. This curious phenomenon was described first by Reuss,[1] working at Moscow, in 1808, and to it has been given the name *electrical endosmose*. Reuss, who employed clay diaphragms in water, noticed that, as the current forced water through the clay toward the negative pole (cathode), there also occurred migration of suspended clay particles in the direction of the positive pole (the anode). This migration of particles in suspension has come in time to be called *cataphoresis*, and the term should be limited to this meaning. There has arisen, however, a great deal of confusion regarding the use of the two expressions, *electrical endosmose* being employed to include

[1] Wiedemann, *Elektricität*, **1**, 1007 (1893).

cataphoresis,[2] and *cataphoresis*, on other occasions, being made in turn to do double service.[3]

Electrokinetic phenomena in two-phase systems of liquid, and solid may be analysed into four distinct processes, of which electrical endosmose and cataphoresis are the ones commonly met with. So far as the electric current is concerned, it is possible to distinguish two cases, as follows:—

(1) *A difference of potential sending a current through the system may produce a relative displacement of the phases.*

(*a*) If the solid is fixed in the form of a porous diaphragm the liquid may be forced through the diaphragm. Electrical endosmose.

(*b*) If the solid is in the form of a suspension and is free to move, the solid may migrate through the liquid. Cataphoresis.

(2) *A relative displacement of the phases may produce a difference of potential and consequently an electric current may flow through the system.*

(*a*) If the solid is fixed in the form of a porous diaphragm through which liquid is forced, a difference of potential and an electric current may be established between the extremes of the diaphragm. Quincke's 'diaphragm current.'

(*b*) If the finely divided solid is dropped through the liquid, a difference of potential and a current may be set up between the upper and lower liquid strata. Billitzer's experiments.[4] This case resembles closely the drop electrode.

Wiedemann[5] is to be credited with the first quantitative study of electrical endosmose, and he was able, as a result, to deduce three empirical generalizations:

(1) The mass of liquid transported in unit time through a porous diaphragm, is directly proportional to the strength of the electric current; and, for a given diaphragm material and given current strength, it is independent of the length and sectional area of the diaphragm.

(2) The difference in hydrostatic pressure maintained by electrical endosmose between the two sides of a porous diaphragm, varies directly as the current strength, and for a given diaphragm material and a given current, is proportional directly to the length and inversely to the sectional area of the diaphragm; it is also proportional to the specific resistance of the liquid in the case of an aqueous solution.

(3) For a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied potential and is independent of the dimensions of the diaphragm.

Quincke[6] forced liquid through an apparatus containing a porous diaphragm and found that differences of potential were produced. He measured these differences and the "diaphragm currents" which

[2] Cf. Patents of Botho Schwerin (Gesellschaft für Elektroosmose).

[3] Cf. Cruse, *Phys. Zeit.*, 6, 201 (1905); Hittorf; *Zeit. Phys. Chem.*, **39**, 613 (1902); **43**, 239 (1903); Morton; *Cataphoresis* (1898).

[4] Drude's *Ann.* **11**, 937 (1903). Cf. Freundlich, *Kapillarchemie*, 230 (1909).

[5] *Pogg.-Ann.*, **87**, 321 (1852); **99**, 177 (1856).

[6] *Pogg.-Ann.*, **107**, 1 (1859); **110**, 38 (1860).

resulted and arrived at the following generalization, which may be regarded as the converse of Wiedemann's third law:

"When water is forced at a certain rate through a porous diaphragm, the difference of potential produced is independent of the dimensions of the diaphragm but is proportional directly to the hydrostatic pressure."

The problem was subsequently taken up by Helmholtz,[7] who developed quantitatively and mathematically an hypothesis which Quincke has previously put forward in a qualitative way. It was suggested that, under most circumstances, solids and liquids become electrically charged when brought into contact. The distribution of charges is such that the surface of the solid is charged oppositely to the more or less mobile layer of liquid next it and with which it is in contact. This orientation of charges gives rise to a so-called electrical double layer. A potential gradient applied externally tends to produce a displacement of the electrically charged layer of liquid (in case the solid is fixed in the form of a capillary tube or diaphragm) and if the liquid is not a perfect insulator, the displacement results in a continuous flow[8] of liquid along the surface of the solid.

Freundlich,[9] following a treatment used by Perrin[10] has developed the following expression for the amount of liquid (V_e) transported in unit time through a porous diaphragm:

$$V_e = \frac{q\epsilon ED}{4\pi\ \eta l} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

In this equation E is the total fall in potential through the diaphragm, D and η are respectively the dielectric constant and the viscosity coefficient of the liquid and ϵ is the potential of the Quincke-Helmholtz double layer at the solid-liquid interface. Since $E = RI$ and $R = l/\ \gamma q$ where R is the total resistance, I is the current strength, l and q refer respectively to the length and cross section of the diaphragm, while γ is the specific resistance of the liquid, equation (1) may be written

$$V_e = R_o \frac{\epsilon\ ID}{4\pi\ \eta\gamma} \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Since for a given liquid and diaphragm at constant temperature, ϵ, η, D and γ are constant, V_e is proportional only to the current, which flows through the diaphragm and the equation stands in agreement with the first of Wiedemann's empirical laws. If one calculates the difference of hydrostatic pressure P_c produced by electrical endosmose equation (3) is the result:

$$P_e = \beta\ 2\ \epsilon\ ED \quad . \quad . \quad . \quad . \quad . \quad (3).$$

where β is inversely proportional to the size of the pores in the diaphragm. D, ϵ, and β being constant for a given diaphragm and liquid at constant temperature, equation (3) is a mathematical statement of Wiedemann's third law.[11]

[7] Wied. *Ann.*, **7**, 337 (1879) et. seq.
[8] Cf. Lamb, *Phil. Mag.*, (5) **25**, 52 (1888).
[9] *Kapillarchemie*, 225 (1909); Cf. Briggs; *Jour. Phys. Chem.* **21** (1917).
[10] *Jour. Chim. Phys.*, 1904.
[11] Cf. Quincke, *Pogg.-Ann.*, **113**, 513 (1861).

2. *Electrical Endosmose with Pure Liquids, Coehn's Rule.*

The early experiments on electrical endosmose taken in conjunction with those on the migration of suspended particles (cataphoresis) made it appear that solids were charged negatively in contact with water. When turpentine was used instead of water, however, Quincke found that conditions were reversed and that such solids as quartz, shellac, silk, clay, asbestos, porcelain, ivory shavings, animal membranes, &c., were electropositive, with the single exception of sulphur. Sulphur weakly electronegative against turpentine, against water was the most strongly electronegative of all the solids which Quincke studied.

Coehn[12] has considered the question raised by these differences, and has proposed the following empirical rule:

When two non-miscible substances, one of which is a pure liquid, are in contact, the substance with the higher dielectric constant is positive against the substance with the lower.

Quincke's data appear intelligible in the light of Coehn's rule. Water and turpentine have dielectric constants of 81 and 5, respectively. Furthermore, the constant in the case of water is one of the largest known and we should expect nearly every substance to be electronegative against water. In contact with turpentine, however, many substances ought to be electropositive, exactly as Quincke found was the case experimentally. Coehn's rule appears to hold fairly well for pure liquids (although there are some weak points in his own evidence)[13], but when applied to aqueous solutions, especially those containing dissolved electrolytes, the rule fails utterly.

3. *Electrical Endosmose with Solutions. Effect of Acids, Bases and Salts.*

In all the early experiments, as we have seen in the preceding sections, water flowed to the cathode. Not only pure water showed this unidirectional tendency, but aqueous solutions appeared to do so as well, the only difference being that the rate of flow was less for solutions than for the pure solvent.[14] Consequently, after the acceptance of the physical theory of the electrical double layer, the belief became general that all solids were charged negatively by contact either with water or with aqueous solutions.

Nevertheless, instances[15] had been recorded where aqueous solutions flowed to the anode rather than towards the cathode. Hittorf[16] found, for instance, that cadmium chloride solutions flowed to the anode through animal membrane but went to the cathode through earthenware, and although Perrin is usually credited with the first definite statement that "reversals" to the anode were possible and could be produced at will by suitable choice of electrolyte

[12] *Wied. Ann.*, **64**, 227 (1893), *Zeit. Elektrochemie*, **16**, 586 (1910).
[13] Cf. Briggs, *Jour. Phys. Chem.*, **21**, 204 (1917).
[14] Porrett, *Thomson's Annals of Philosophy*, **8**, 74 (1816); Daniell, *Phil Trans.*, **129**, 97 (1839); Gernez, *Comptes rendus*, **89**, 303, 348 (1879).
[15] Wiedemann, *Elektricitat*, **2**, 153 (1883); Gore, *Proc. Roy. Soc.* **31**, 253 (1880)
[16] *Zeit. Phys. Chem.* **39**, 613 (1902); **43**, 239 (1903).

in solution, the point was really established with remarkable clearness by Parker.[17]

Perrin's contribution[18] to what was still an obscure phenomenon, did, however, constitute a great step forward. He devised an apparatus which enabled him to employ many different powdered substances in the form of pervious diaphragms. Turning his attention to the effect of dissolved substances and using extremely dilute solutions (never more concentrated than N/50 and usually about N/500), he concluded first that *electrolytes* alone among solutes influenced the course of electrical endosmose and that the ions had a specific effect. Hydrogen and hydroxyl ions proved particularly active. With a diaphragm of insoluble chromic chloride, for example, dilute alkalies flowed to the cathode whilst dilute acids flowed to the anode—a clear cut reversal. Similar acid alkali reversals were found with alumina, carborundum, sulphur, gelatine, graphite, naphthalene, etc., although none was observed with cotton wool, glass and iodoform. Whenever reversal did occur, there was a certain hydrogen ion concentration at which no flow at all occurred, this point corresponding approximately to an isoelectric condition of the diaphragm.[19]

Since flow to the cathode indicated an electronegative diaphragm, whilst flow to the anode pointed to an electropositive one, Perrin concluded as follows:—

'The electric potential of any surface whatever in aqueous solution is invariably increased [made more positive or less negative] by the addition of a monobasic acid and is invariably lowered [made more negative or less positive] by the addition of a non-acid base.'

Perrin considered next a large number of other ions. He found that, excepting hydrogen and hydroxyl, none of the common univalent ions was of much influence on electrical endosmose. Polyvalent ions were more active. Briefly, the results may be summarized in the following statement, sometimes referred to as Perrin's valence rule, which one should compare with the Schulze-Hardy rule of flocculation:

Every diaphragm tends to become charged positively in an acid solution and negatively in an alkaline one. Every ion of unlike sign tends to neutralize the charge on the diaphragm and this tendency increases rapidly with the valence.

Perrin's rule has been extended to alcoholic solutions by Baudouin[20], incompletely to liquid ammonia by Ascoli[21] and by Guillaume[22] to the so-called Bose-Guillaume phenomenon.

Morse and Horn[23] have made use of electrical endosmose to remove air from the pores of porous cups, before impregnating the

[17] *Johns Hopkins Dissertations*, **31**, 23 (1901); Cf. Briggs, *Jour. Phys. Chem.* **21**, 235 (1917).
[18] *Jour. Chem. Phys.* **2**, 601 (1904).
[19] Cf., however, Bethe and Toropoff, *Zeit. Phys. Chem.* **89**, 597 (1915).
[20] *Comptes rendus*, **138**, 898 (1904).
[21] *Comptes rendus*, **137**, 1253 (1903).
[22] *Ibid.* **147**, 53 ('908); Cf. Briggs: Jour. Phys. Chem. **21**, 215 (1917). *Amer. Chem. Jour*, **26**, 801 (1901).

latter with copper ferrocyanide. This led Frazer and Holmes[24] to carry out experiments with an elaborate electro-osmometer, in which they noticed the usual acid-alkali reversals and concluded that the effect of the ions bore some relation to their migration velocities. Coehn[25] has also carried out some interesting electro-osmotic measurements with a Pukall filter and solutions of H_2SO_4, $CuSO_4$, HNO_3, acetic acid, alkali metal sulphates, alkali and heavy metal nitrates.

Barratt and Harris[26] in some excellent work with diaphragms of gelatine, agar, and parchment, have confirmed in the main the valence rule of Perrin. Their data suggest the problem of finding out what effect the salts of Hofmeister's series would have on endosmose through gelatine and other albumenoids. Recently this question has been investigated by Bethe and Toropoff[27] and although the data are incomplete, there is reason to believe that the lyotrope series really does play an important part.

An elaborate study of electric endosmose in neutral solutions has been completed by Elissafoff[28] in Freundlich's laboratory. The procedure was based on Lemström's[29] method of measuring endosmetic movements in a single capillary without the direct application of electrodes. Elissafoff's data show that Perrin's valence rule holds only to a limited extent. So far as the alkali metal and alkaline earth metal cations are concerned the valency rule holds satisfactorily,[30] but fails in the case of heavy metal and organic cations. For example, certain univalent organic cations appeared quite as effective in neutralizing the charge (see the second part of Perrin's rule) on negative glass or quartz as did the divalent light metal cations. Silver as ion belonged to the divalent metals; mercuric chloride was as effective as aluminum sulphate and far more so than chlorides of the divalent alkaline earths. That the anion is also active was demonstrated by experiments with potassium benzoate and sodium picrate, these anions restraining the tendency of the potassium or sodium to neutralize the negative charge on the walls of the capillary.

No reversal by acids was observed, but the strength of the solutions employed was never greater than one ten-thousandth normal. With certain salts, however, reversals were obtained. Against solutions of thorium nitrate of sufficiently high concentration the glass or quartz became electropositive and a similar reversal occurred with solutions of methyl violet, a basic dye. One should compare this with what Larguier des Bancels[31] found with wool and basis dyes, where the latter showed a striking tendency to make the wool positive.

[24] *Amer. Chem. Jour.*, **40**, 319 (1908); H. N. Holmes, *Dissertation* (*Johns Hopkins*, 1907).
[25] *Zeit. Elektrochemie*, **16**, 586 (1910).
[26] *Zeit. Elektrochemie*, **18**, 221 (1912); *Biochemical Jour.*, **6**, 315 (1912).
[27] *Loc. cit.*
[28] *Zeit. Phys. Chem.* **79**, 385 (1912).
[29] *Drude's Ann.*, **5**, 729 (1901).
[30] Freundlich and Elissafoff have employed electro-osmosis to estimate the valency of radium. The results agree with the assumption that radium is a divalent metal belonging to the alkaline earth group. *Phys. Zeit.*, **14**, 1052 (1913).
[31] *Comptes rendus*, **149**, 316 (1909).

4. Theories of Electrical Endosmose. Contact Electrification and Adsorption.

Wiedemann believed that the electric current exerted a tractive action upon the liquid in a capillary tube and that the liquid was carried thus from anode to cathode, regardless of the substance composing the walls. In opposition to this view, Graham,[32] Quintus Icilius and Breda and Logemann,[33] showed conclusively that no transport of liquid occurred unless a diaphragm or its equivalent were present. As I observed in the earlier pages of this paper, we owe to Quincke and to Helmholtz the electrical double layer theory of contact electrification. The Coehn rule is an interesting development of this theory. But both Quincke and Helmholtz contributed little to further our understanding of why and how an electrical double layer or its equivalent may be formed when solid and liquid are placed in contact.

For the special case of a metal in contact with its own ions in solution the Nernst theory holds. It is only natural that there should have been proposed an analogous explanation of the contact potentials of non-metallic solids. Every solid dissolves in water to a certain extent and the electrical double layer might be supposed to be produced by differences in the rates of ion diffusion—if the cation diffused faster, a separation of charges would tend to occur and the solid (or liquid immediately in contact with the solid) would become negative. Bredig[34] has given vague expression to this idea by observing that the Coehn rule points to some relation between solubility of ions in different media and the dielectric constant.

As a matter of fact, the explanation outlined above cannot be the correct one for the case of a solid immersed in a pure liquid, unless one postulates that the liquid remains unsaturated with respect to the solid or that fresh liquid is being supplied constantly. The electrical charge does not disappear when the liquid is saturated with the particular solid, although its sign and intensity may change, while the potential difference at the liquid interface in a concentration cell exists only so long as a difference in concentration is maintained. No *permanent* potential difference can possibly be produced as the result of unequal ion mobilities. Perrin has offered an explanation of his acid-alkali rule by postulating that, since hydrogen and hydroxyl ions are abnormally mobile, they are correspondingly small, and are able thereby to crowd to the surface of a solid more closely than the other ions. This might account for the solid being positive in acid and negative in alkaline solutions. Perrin was unable, nevertheless, to reconcile his theory with all the facts, for he observed that lithium bromide failed to charge a chromic chloride diaphragm negatively although bromine ions are twice as mobile as lithium ions.

Haber[35] has suggested for the particular case of glass against water that the solid is essentially a hydrogen electrode, and that the

[32] (2) *Phil. Mag.* (4) **8**, 151 (1854).
[33] (3) *Pogg. Ann.*, **100**, 149 (1857).
[34] *Zeit. Elektrochemie*, **9**, 738 (1903).
[35] *Haber and Klemensiewicz, Zeit. Phys. Chem.*, **67**, 413 (1909).

magnitude of the potential difference depends upon the concentration of hydrogen ions in solution. Guided by Haber's theory, Cameron and Oettinger[36] performed some rather inconclusive experiments on the potential produced by acid and alkaline solutions forced through a capillary of glass. Haber's theory, as Freundlich points out, is open to the serious objection that electrical endosmose does not depend entirely upon hydrolysis of the dissolved solute, as it should do if the concentration of hydrogen ions is the only factor. Acidity and alkalinity, while of very great influence, are not the only factor determining electro-osmotic effects.

Freundlich[37] was the first to point out clearly the intimate relations existing between adsorption and electrical endosmose. This development may be said to be the result of his own work on adsorption and the speculation of Perrin[38] regarding the analogies between the behaviour of suspensions and the peculiarities of electrical endosmose. Freundlich went still further than Perrin. He had already shown the relation between adsorption and the stability of suspensions and had pointed out the validity of the Schulze valence rule for adsorbed light-metal cations and the ordinary anions. He had discovered, too, that many organic ions as well as the heavy metal cations were exceptions to the Schulze rule. He was able, as a result, to emphasize the similarity between the Schulze rule and the valence rule of Perrin, and, from Elissafoff's data, he showed that exceptions to Schulze's rule were exceptions likewise to Perrin's. From this it was only a step forward to apply to electro-osmotic phenomena a definite theory based upon adsorption, or more specifically, upon the selective or preferential adsorption of ions.

Freundlich called the difference of potential between solid and solution, the "adsorption potential." If a cation is adsorbed to a greater extent than the accompanying anion, the solid becomes positively charged, and if it is employed as a diaphragm, the electrical endosmose will occur from cathode to anode. For the case of a solid against pure water it is only necessary to postulate selective adsorption, either of the ions already present in water or produced by the solid dissolving. When preferential ion adsorption occurs, the number of ions actually adsorbed is very small, because the charge on a single ion is relatively large and the electrical double layer that is established opposes any further spatial separation of positive and negative ions.

Freundlich[39] has recently modified his original theory of the adsorption potential, without improving matters appreciably and not without adding several complicating hypotheses. He suggests that the contact potential of the diaphragm depends upon the nature of the material of which it is composed (upon differences in solution tension of the ions thrown out) and that it is affected only indirectly by adsorption. In my opinion contact potential does undoubtedly depend upon the nature of the solid itself, but the important thing

[36] *Phil. Mag.* (6), **18**, 586 (1909).
[37] *Kapillarchemie*, 245, (1909); *Zeit. Phys. Chem.* **79**, 407 (1912).
[38] *Jour. Chim. Phys.*, **3**, 85 (1905).
[39] Freundlich and Elissafoff, *Zeit. Phys. Chem.*, **79**, 407 (1912).

is the power of the solid to adsorb selectively the ions present in the liquid from the beginning, or produced by the solid dissolving.[40]

Frazer and Holmes[41], following a suggestion rejected by Whetham[42], have advanced a distinctly different hypothesis based upon the solvate theory. If the hydration of the cation is greater than that of the anion, for example, liquid should be carried from anode to cathode; and this is what the authors found to be the case with neutral salts of the alkalies against earthenware. Since the mobility of an ion might be regarded as an inverse measure of its hydration, one could expect a strong flow to the cathode in an alkaline solution and a strong flow to the anode in an acid solution. This deduction agreed with the facts as far as they were determined by Frazer and Holmes. Barratt and Harris, who favoured a similar theory, were rather overwhelmed by its consequences, for they calculated that anywhere between 18 and 370 molecules of water were transported through agar diaphragms for every molecule of solute decomposed electrolytically.[43]

The solvate theory of Frazer and Holmes cannot be correct, for one would have to conclude, in consequence, that there is a fundamental difference between electrical endosmose and Quincke's diaphragm currents. Moreover the theory assigns to the diaphragm a subordinate and purely mechanical rôle. Neither does it explain why mere traces of lanthanum salts, for instance, reduce the flow of an alkaline solution, or why an acid solution *flows to the cathode* through powdered glass. If there is any relation between endosmose and ion mobility, it is better to consider it an indirect one, produced by a possible relation between ion mobility and ion adsorpton, as I pointed out when discussing Perrin's speculations.

After careful consideration of the facts in the case, it would appear that the most satisfactory working hypothesis to account for contact electrification of this type (and hence to serve as basis to an understanding of electrical endosmose and cataphoresis) is the one proposed originally by Freundlich and emphasized recently by Bancroft.[44]

By virtue of their surface properties solids are able to adsorb substances from a liquid with which they are in contact. They may adsorb a particular ion preferentially, in which case we have selective ion adsorption and either a positive or a negative charge on the solid. The adsorbing substance tends to be peptised by the adsorbed ion.

[40] The modified Freundlich theory of the ionization of colloid aggregates, according to which particles of a basic nature, such as ferric hydroxide, are believed to give off OH ions to the liquid and become positively charged, while particles of acid nature, such as silica, give up H ions to the liquid and become electro-negative. The suggestion has received the support of Zsigmondy and many others. While it is easy thus to account for the charge borne by substances such as silica and ferric hydroxide, it is by no means so simple to do so with substances such as sulphur, carborundum, and diamond, all of which are charged electrically when placed in contact with water or suitable aqueous solutions. Compare Burton, *The Physical Properties of Colloid Solutions* (1916).

[41] *Am. Chem. Jour.*, **40**, 319 (1908).

[42] *Theory of Solution*, 292 (1902).

[43] In connection with Frazer and Holmes' theory, see Bethe and Toropoff, *Zeit. Phys. Chem.*, **89**, 597 (1915).

[44] *Jour. Phys. Chem.*, **16**, 312 (1912); *Trans. Am. Electrochem. Soc.*, **21**, 233 (1913).

Or solid may adsorb the solvent itself and be peptized, while the other possibilities, all of which tend to produce peptization, are adsorption of a non-electrolyte, an indissociated salt, or a second colloid.[45] Since electrical endosmose has to do with electrically charged surfaces, we are concerned chiefly with preferential adsorption of ions.

It is necessary to postulate that every solid has a specific adsorbing power for a given ion, depending upon the specific surface[46] of the solid, upon the temperature, upon the concentration of the particular ion in the solution and upon the other ions present, or adsorbed previously by the solid. When the ion content of a liquid is vanishingly small, we shall have but little ion adsorption and little electrical endosmose. On the other hand 'pure' water shows marked endosmose through many diaphragms. This is a case of preferential ion adsorption where the ions are produced both from the ionization of water itself and the solution of the solid, which is a very important matter in some cases (notably glass).[47] Since the majority of solids are charged negatively against water, hydroxyl ions are probably adsorbed in preference to hydrogen ions. In discussing the potential of a solid against water *originally pure*, we must accordingly take two factors into account.[48]

(1) The specific adsorption capacity of the solid for hydrogen and hydroxyl ions produced by the dissociation of water.

(2) The dissolution of the solid, which, though extremely slight in many cases, may produce ions that are strongly adsorbed.

Hydrogen ions are often adsorbed preferentially from solutions containing them, especially from acids, though we have seen that the rule is by no means a general one. Experiments by the author have shown that aluminum, which is positive in dilute hydrochloric acid, is weakly negative in citrate acid where the equivalent selective adsorption of the citrate ion must be greater than that of the hydrogen ion. Moreover, we know that metal sulphides are peptized by hydrogen sulphide, an acid, yet the adsorbed ion is sulphur and not hydrogen; for the particles in suspension are electro-negative.[49]

In general the same statement applies to the adsorption of hydroxyl ions. Solids seem to have a somewhat greater adsorption affinity for hydroxyl ions than for hydrogen ions, though there are notable exceptions to this generalization. The general theory covering the electrical endosmose of all liquids and solutions may be formulated as follows:—

(1) Electrical endosmose depends upon the preferential or selective adsorption of ions and is influenced only by those ions which are adsorbed by the diaphragm.

[45] Cf. Bancroft, *Jour. Phys. Chem.*, **20**, 85 (1916).

[46] Wo. Oswald, *Grundriss der Kolloidchemie*, 29 (1912).

[47] Cf. Briggs, Bennett, and Pierson, *Jour. Phys. Chem.*, **22**, 256 (1918); *Trans. Am. Electrochem. Soc.*, **31**, 257 (1917).

[48] In this connection, compare the statement of Schwerin, Brit. Pat. 10793 (1909) wherein he emphasises the importance of taking into account the dissolving of the diaphragm.

[49] Winssinger, *Bull. Soc. chem.*, Paris (3), **49**, 452 (1881); Linder and Picton, *Jour. Chem. Soc.*, **61**, 116 (1892).

In this connection compare the beautiful experiments of Lottermoser, *Jour. prakt. Chem.* (2), **72**, 53 (1905).

(2) Any circumstance or condition which changes the adsorption produces an effect upon electrical endosmose. Electrical endosmose varies, therefore, with the condition of the surface (for a given solid), with the relative and absolute ion concentrations, with the temperature and so forth.

(3) The *direction* of endosmose indicates the sign of the diaphragm; the *rate* of endosmose is proportional to the intensity of the charge on the diaphragm in case the potential gradient through the diaphragm is constant. When the liquid flows to the cathode, the diaphragm is negative; when it flows to the anode the diaphragm is positive. No flow at all probably indicates an iso-electric condition.[50]

(4) A diaphragm tends to become positive by the selective adsorption of cations, and negative by the adsorption of anions.

(5) The positive charge produced by an adsorbed cation is neutralized more or less by the addition of an adsorbed anion, the effect increasing with the concentration of the anion. Similarly, the negative charge produced by an anion is neutralized by an absorbed cation.

(6) Electrical endosmose measures the tendency of a solid to form an electrical suspension in a given liquid, but it does not measure the tendency of the solid to form a non-electrical suspension, such as is produced by adsorbed solvent, solute or neutral colloid.[51]

5. *Adsorption Potential, Temperature and other Factors.*

Returning to equation 1 it is hardly necessary to point out that ϵ, representing the potential of the Quincke-Helmholtz double layer, stands also for the ' adsorption potential ' of the solid-liquid interface. Quincke and also Von Tereschin have calculated values[52] of ϵ for a glass-water interface, using data obtained by electro-osmotic experiments with capillary tubes. The values lie close to 50 millivolts and are of the same order of magnitude as those[53] calculated from the migration velocities of particles suspended in water (cataphoresis).

From the beginning it has been recognized that electrical endosmose is greatly affected by changes of temperature. Perrin found that, with rising temperature, the volume of liquid transported under otherwise constant conditions increased very rapidly, and he reported *that temperature had about the same effect on the rate of endosmose as it had on the fluidity (reciprocal of viscosity) of the liquid.* Equation 1 indicates that this condition is plausible (since D does not change rapidly with the temperature), provided ϵ remains practically constant as the temperature changes. Perrin's conclusion that the

[50] Note that Berthe and Toropoff maintain that the ' indifferent ' point (zero flow) and the isoelectric point do not necessarily coincide exactly. *Zeit. Phys. Chem.*, **89**, 597 (1915).

[51] Schwerin has applied this principle in Brit. Pat. 2379 (1911), where in order to obtain stable suspensions he adds acids to those substances which migrate to the cathode and bases to those which migrate to the anode. In 27930 (1911) he adds absorbed positive or negative colloids (alumina, humic acid, silica, etc.) to obtain the same results.

[52] Data compiled by Burton, *Physical Properties of Colloid Solutions*, 135 (1916).

[53] Freundlich, *Kapillarchemie*, 227 (1909).

temperature coefficient of viscosity determines very largely the value of the temperature coefficient of electro-osmose, is strengthened by experiments of Coehn and Raydt,[54] Cameron and Oettinger,[55] and of Briggs, Bennett and Pierson.[56]

On the other hand Cruse[57] found an apparent maximum in the rate of electro-osmose, this maximum occurring between 35° and 40° C. Briggs, Bennett, and Pierson have shown that Cruse's maximum was probably due to the diaphragm not being in equilibrium with the liquid phase. They have carried out determination of the temperature coefficient and find that with diaphragms of asbestos, cellulose (filter paper) and carborundum, the rate of flow increases with rising temperature slightly less rapidly than the viscosity decreases; the rate for a given diaphragm at constant temperature is also very exactly proportional to the applied external potential. It is only fair to point out, however, that since adsorption varies with the temperature and since the temperature coefficients for anion and cation are not necessarily equal, ε may also vary with the temperature and might even change its sign. In the cases just discussed, ε is probably very nearly constant.

6. *Related Phenomena.*—Cataphoresis is the reverse of electrical endosmose. One is dealing here with a mobile or "floating" diaphragm. The fundamental theory is without question the same; such differences as appear to exist between the two processes being due, in all likelihood, to flocculation complicating the phenomena of cataphoresis. The particles are positive if they migrate to the cathode, negative if they migrate to the anode. Acid-alkali reversals are known, and strongly adsorbed ions determine the charge on the particles. As the subject constitutes a separate report in this series, it will not be considered further at this time.

Perrin[58] has pointed out that the curious Bose-Guillaume phenomena is a special case of Quincke's "diaphragm currents," and is an electro-osmotic phenomenon. Guillaume's data[59] are evidence in favour of the adsorption theory. Electro-stenolysis is another phenomenon dependent upon contact electrification.

When certain aqueous solutions are separated from water by a porous plate of porcelain, for instance, a slight but measurable osmosis is often observed. In some instances the osmotic flow occurs from the solution into the water and not from the water into the solution as one would expect it to do. Such apparently abnormal osmosis is termed "negative osmose."[60]

According to Bartell the most plausible way of accounting for osmosis of this type is to assume that it is caused by the "polarization" of the membrane. The membrane being in contact with different liquids, the adsorption potential will be different for each

[54] *Drude's Ann.*, **30**, 797 (1909).
[55] *Phil. Mag.* (6) **18**, 586 (1909).
[56] *Jour. Phys. Chem.* **22**, 256 (1918).
[57] *Phys. Zeit.*, **6**, 201 (1905).
[58] *Comptes rendus*, **147**, 55 (1908).
[59] *Ibid.* **147**, 53 (1908).
[60] Bartell, *Jour. Am. Chem. Soc.*, **36**, 646 (1914); Bartell and Hocker, *Jour. Am. Chem. Soc.*, **38**, 1029 (1916); Freundlich, *Zeit. Kolloidchemie*, **18**, 11 (1916); Girard, *Comptes rendus*, **146**, 927 (1908); **151**, 99 (1910) *et. seq.*

face and there will be established a difference of potential between the ends of the capillaries. This difference in potential causes electrical endosmose to take place in one direction or the other and an apparent osmotic action results. That a difference of potential really does exist between the water side and the solution side of the diaphragm has been demonstrated experimentally. The explanation outlined above is an ingenious one, but the problem is by no means solved as yet.[61]

Summary.

Electro-osmotic phenomena with pure liquids and solutions have been described and the various theories discussed critically. The most plausible hypothesis seems to be the Freundlich-Bancroft theory of selective ion adsorption. The effect of temperature changes and other influences have been considered and in conclusion mention has been made of negative osmosis and other phenomena related closely to electrical endosmose. Cataphoresis and electro-stenolysis have not been included.

Recent Papers on Electrical Endosmose.

'Electric osmosis and concentration of electrolytes.' J. O. Wakelin Barratt and Albert B. Harris, *Zeit. Elektrochemie*, **18**, 221 (1912).

Authors have studied electrical endosmose through diaphragms of gelatin, parchment and agar. Rate of flow and direction of osmose appear to be determined by the nature and valence of the ions in solution. See next reference for more comprehensive article.

'Electro-osmosis.' J. O. Wakelin Barratt and Albert B. Harris, *Biochemical Jour.*, **6**, 315 (1916).

See preceding reference. Article gives data for a large number of diaphragm substances, describes ingenious apparatus and discusses the hydration theory. Electro-osmose into human forearm studied.

'The effect of electrolytes on electrical endosmose.' G. von Elissafoff, *Zeit. Phys. Chem.*, **79**, 385 (1912).

Very important article showing where Perrin's valence rule holds and where it fails. In an appendix written with Freundlich, the author argues very effectually in favour of the ionic absorption theory.

'Electrical endosmose.' Wilder D. Bancroft, *Jour. Phys. Chem.*, **16**, 312 (1912); *Trans. Am. Electrochem. Soc.*, **21**, 233 (1912).

Proposes ionic absorption hypothesis and applies it to some hitherto unexplained experiments of Reed, *Trans. Am. Electrochem. Soc.*, **2**, 238 (1902). Article includes discussion of addition agents in electroplating.

'Determination of the valence of radium by means of electrical endosmose.' Herbert Freundlich and G. von Elissafoff, *Phys. Zeit.*, **14**, 1052 (1913).

Radium appears to be divalent and closely related to barium. Method depends upon application of Perrin's rule and requires less than 0·01 milligram of substance.

'Hydration of organic colloids under the influence of electrolysis.' E. Doumer, *Comptes rendus Soc. Biol.*, **76**, 40 (1914).

Some curious hydration and dehydration effects observed during electrical endosmose with gelatin.

'Negative osmose.' F. E. Bartell, *Jour. Am. Chem. Soc.*, **36**, 646 (1914).

Author accounts for positive and negative osmosis through porcelain by assuming that selective adsorption polarises the membrane and that the osmosis is really electrical endosmose.

[61] Cf. Bancroft. *Jour. Phys. Chem.*, **21**, 441 (1917).

'Electrolytic endosmose.' HORACE G. BYERS and CARL H. WALTER, *Jour. Am. Chem. Soc.*, **36**, 2284 (1914).
Complicated endosmotic experiments with three and six compartment cells.

'Electrolytic processes of diaphragms.' I. Disturbance of Neutrality. ALBRECHT BETHE and T. TOROPOFF, *Zeit. Phys. Chem.*, **88**, 686 (1914).
With organic diaphragms electro-osmose causes H^+ concentration to decrease at anode side and increase at the cathode side. Electrolytes in solution affect the speed with which the neutrality is disturbed. The order of anions and cations recalls the Hofmeister series.

'Electrolytic processes at diaphragms.' II. The dependence of the magnitude and direction of the concentration changes and the water movement upon the hydrogen ion concentration. A. BETHE and T. TOROPOFF, *Zeit. Phys. Chem.*, **89**, 637 (1915).
Article includes a number of experiments on electrical endosmose with gelatin, albumin, collodion, animal and other membranes. Interface potential is an ionic adsorption phenomenon; electrical endosmose depends both upon interface potential and the relative hydration of mobile ions.

'The relation of osmose of solutions of electrolytes to membrane potentials.' Theoretical. F. E. BARKER and C. D. HOCKER, *Jour. Am. Chem. Soc.*, **38**, 1029 (1916).
Author combines ionic adsorption theory with Nernst diffusion theory to account for polarization of membrane.

'The osmose of some solutions of electrolytes with porcelain membranes and the relation of osmose to membrane potential.' F. E. BARTELL and C. D. HOCKER, *Jour. Am. Chem. Soc.*, **38**, 1036 (1916).

'Negative osmosis.' HERBERT FREUNDLICH, *Zeit. Kolloidchemie*, **18**, 11 (1916), (Original article not available.)

1917.

'Electrical endosmose,' I. T. R. BRIGGS, *Jour. Phys. Chem.*, **21**, 198 (1917).
Complete historical summary with references to literature. Critical study of different theories of electro-osmose and contact potentials. Author prefers ionic adsorption hypothesis of Freundlich and Bancroft.

'Electrical endosmose and adsorption.' T. R. BRIGGS, H. L. PIERSON, and H. S. BENNETT, *Trans. Am. Electrochem. Soc.*, **31**, 257 (1917).
See below.

1918.

'Electrical endosmose,' II. T. R. BRIGGS, H. S. BENNETT, and H. L. PIERSON, *Jour. Phys. Chem.*, **22**, 256 (1918).
Author describe new and convenient electro-osmometer and study the relation between the rate of endosmose and voltage, temperature and other factors. Data tend to confirm ionic adsorption theory.

ELECTRICAL ENDOSMOSE. II. INDUSTRIAL APPLICATIONS.

By T. R. BRIGGS, *Cornell University*.

INTRODUCTION.

During recent years increasing attention has been paid to the possibility of making some practical application of electro-kinetic processes, including electrical endosmose.[1] It is proposed in this report to indicate to what extent and in what direction these industrial applications have been attempted and to elucidate, wherever necessary and whenever possible, the principles involved. Owing

[1] Cf. Foerster: *Elektrochemie*, 116 (1915); Kruyt: *Chem. Weekblad*, **14**, 766 (1917); *Chem. Abstr.*, 11, 2984 (1917); ewis: *Jour. Soc. Chem. Ind.*, **35**, 575 (1916)

to the close relationship existing between electrical endosmose and cataphoresis and because of the not very surprising fact that cataphoresis plays a very important part in many so-called "electro-osmotic" processes in practice, no attempt will be made to exclude technical cataphoresis from this discussion or to limit it strictly to electrical endosmose.

Dewatering Peat by Electrical Endosmose.

The possibility of using electrical endosmose and cataphoresis in the removal of water from muds, pulps and jelly-like or spongy masses containing materials in suspension, has been considered in some detail during recent years, especially by Count Botho Schwerin in Germany. The peat bogs of the latter country and of Ireland offer a very great potential source of fuel provided only a sufficiently economical method can be devised for dewatering the material. Filtration and centrifuging are not applicable because of the slimy nature of the peat pulp, which causes an impervious layer to form on the filter or in the centrifuge. Attempts have been made to submit the peat mud to stream evaporation combined with drying in the air. The mud as it comes from the bog contains approximately 90 per cent. of water and to evaporate a pound of this material containing 50 per cent. of water (which can then be cut into blocks and dried in the air) approximately 880 B.T.U. are required. After air-drying the intermediate 50 per cent. material, a final product results, containing about 20 per cent. of moisture and possessing a calorific power of about 8100 B.T.U. per pound. As one pound of the original mud yields rather less than one-eighth pound of dried peat, yielding not more than 1000 B.T.U., it is evident at once that the problem cannot be solved by a direct dehydration process such as the one outlined above. But it might be possible in such a duplex process to substitute electro-osmose for the preliminary evaporation and so either to remove mechanically a large part of the water or else to concentrate the suspended particles in the pulp by causing them to migrate by cataphoresis to the electrodes. It is well to bear in mind, in this connection, that the electro-osmotic process cannot possibly *dry*[2] anything; it can at best remove water only to the extent that filter presses or centrifuges do.

Count Schwerin was granted his first British Patent[3] in 1900. Various types of apparatus were disclosed, in all of which the peat was treated between a suitable anode and a perforated cathode. On passing a direct current between the electrodes, water was forced out of the spongy or semi-liquid mass and escaped through the perforations in the cathode. At the same time some of the suspended peat migrated to the anode and formed there a fairly dense layer. Schwerin called this the "motorial" action of the electric current.

He next patented an apparatus[4] consisting of a series of superposed horizontal partitions, corrugated to allow liquids to flow away, and supporting boxes containing raw peat. These boxes were filled

[2] Cf. Nernst and Brill: *Verh. Deutsch. phys. Ges.*, 11, 112 (1909).
[3] Brit. Pat., 12431 (1900).
[4] Brit. Pat. 22301 (1901)

with pervious metallic bottoms serving as cathodes and the anodes pressed down from above upon the peat. The Höchst Color Works experimented with Schwerin's process on a semi-commercial scale and took out several additional patents[5] on improvements of apparatus and procedure. Other patents were taken out in Great Britain by Siemens and Halske,[6] Doull,[7] Kittler,[8] Verey and Downes,[9] and Simm,[10] although the last-named inventor really used the current for heating purposes only.[11]

Schwerin,[12] addressing the Bunsen Society at the Fifth International Congress at Berlin in 1903, discussed some of the preliminary experiments made with his process and attracted at the time a good deal of attention. Starting with a peat mud containing originally nearly 90 per cent. moisture, it was claimed that a volume of water equal to three-fourths the volume of the mud could be removed and that this could be done with an expenditure of only one-fifth part of the energy available in the recovered peat. The most suitable potential gradient through the peat was stated to be 4 or 5 volts per centimetre and 13 to 15 kilowatt-hours were required in removing one cubic metre of water. Unfortunately, the peat obtained at the end of the treatment contained as high as 65 per cent. of moisture, although the material itself was easily amenable to moulding into bricks or other shapes. It was therefore necessary to subject the moulded peat to prolonged and tedious drying in the air, in order to reduce the water content to the permissible maximum of 20 per cent.

Promising as Schwerin made his process appear, it proved a failure when tried out on a commercial scale apparently because air-drying the material with 65 per cent. moisture proved to be far more tedious and costly than experience with 50 per cent. material had led those interested to expect.[13] Nevertheless, it is possible that the method may some day prove feasible if the electro-osmotic treatment can be improved to yield a product with less than 50 per cent. of moisture; such an improvement might be brought about, as Foerster suggests, by previously disintegrating[14] the jelly-like aggregates in the original peat and thus permitting closer packing of the peat solids. A very large proportion, however, of the water in peat is *adsorbed*, and the difficulty as I see it lies in the removal of this adsorbed moisture; only water held *mechanically* can be removed by electro-kinetic processes.[15]

In recent years Schwerin has endeavoured to improve things by applying to his purposes some of the newer knowledge gained from

[5] Brit. Pats., 3795, 24670 (1904) Farbwerke, vorm. Meister Lucius u. Brüning.
[6] Brit. Pat., 14195 (1903).
[7] Brit. Pat., 1717 (1903).
[8] Brit. Pat., 126 (1904).
[9] Brit. Pat., 2226 (1907).
[10] Brit. Pat., 4792 (1905).
[11] Cf. Davis: *Bull. U.S. Bur. of Mines*, 16, 122 (1912).
[12] *Ber. V. int. Kong. angew. Chem.*, 4, 653 (1908); *Zeit. Elektrochemie*, 9, 739 (1903).
[13] Cf. Foerster: *Elektrochemie*, 118 (1915).
[14] Cf. Brit. Pats., 6993, 6995 (1914).
[15] The same difficulty arises in the removal by cataphoresis of iron oxide from clay. Cf. the "osmose" process of clay purification

the researches of Perrin and others. By adding a trace of caustic alkali to the peat mud, the dewatering is greatly hastened.[16] He has also devised an interesting electro-osmotic filter press[17] in which peat or clay are dewatered under pressure between filter diaphragms and an electric current sent through. It is claimed that by continuous pressure and electrical endosmose, the pressure necessary to filter clay or peat suspensions may be reduced twenty fold. Further improvement is said to be gained by disintegrating[18] in a ball mill the peat as it comes from the bog and adding the electrolyte to the mill.

The "Osmose" Process of Purifying and Dewatering Clay.

The electro-osmose process was next applied to the dewatering and purification of clay,[19] for the purpose of transforming a low grade and impure material into something approximately in quality ball-clay or china-clay. In the older processes the impure clay is first made into a thin slip with water, the slip is allowed to stand until the coarser particles (usually silica) have had time to settle, and the fine particules of clay still remaining suspended in the slip are removed by gravity settling, filtration or centrifugal separation. The settling process is very tedious, and the difficulties of filtering or centrifuging are very great.

Schwerin proposed to hasten and improve the process by dewatering the suspended clay by means of cataphoresis. The crude clay substance is made into a slip with water in the usual way, the kaolin is deflocculated (peptized) by the addition of a little sodium hydroxide or other agent such as humus or sodium silicate, and the coarser particles are allowed to settle. If the impurities such as silica or iron oxide happen to consist of relatively coarse particles unadsorbed by the clay itself or even if they are finely divided but are not deflocculated (peptized) by the addition of agents, the crude clay is purified to a certain extent and is usually improved in plasticity and firing qualities. The clay suspension, after settling, is pumped into the "osmose" machine where it is dewatered by cataphoresis.

According to Ormandy[20] the "Osmose" machine consists of a semi-circular trough, in the centre of which a revolving metal drum serves as anode and outside of this drum and distant about half an inch from it is a cathode of wire netting, surrounding the anode drum on the under side. When the suspension is pumped between the electrodes, the impurities are said to settle on or under the wire cathode, whence they are removed, while clay is deposited on the slowly revolving drum in a blanket 4½ feet wide and ¼ inch thick, containing not more than 20 per cent. of moisture. For other details

[16] Cf. Brit. Pats. 3364, 11626 (1911).

[17] Cf. Brit. Pats. 14369, 23545, 24666 (1912); 10873 (1913); Ulzer: *Zeit. angew. Chem.*, **28** (1), 308 (1915).

[18] Brit. Pats. 6993, 6995 (1914).

[19] Cf. Brit. Pats. 10024 (1907); 28185 (1911) and others.

[20] *Brit. Clayworker*, **22**, 9 (1913); *Pott. Gaz.*, **38**, 1162 (1913); **40**, 178 (1915). Cf. Stoermer; *Tonindustrie Zeit.*, **36**, 178 (1915): also Hopkins. *Brit. Clayworker* **22**, 62 (1913), Cf. Brit. Pats. 725 (1912); 3434 (1913), etc.

as to operation, size of plant, costs and other matters, Ormandy's article and the interesting discussion on the part of members of the Ceramic Society should be consulted.

Among the advantages claimed for the method are (1) greater ease and steadiness of operation; (2) smaller plant-space; (3) lower labour cost; (4) process not only dewaters clay but purifies it as well, thus supplementing the preliminary settling treatment; (5) clay after treatment is very plastic and sinters at a temperature far below the melting point.[21]

Schwerin's " osmose " method has been discussed critically by Bleininger[22] who points out that the " osmose " machine is merely a substitute for the filter press or centrifuge, having the advantage over most filter apparatus of being automatic and continuous. By experiments of his own Bleininger assured himself that no measurable purification occurred during the cataphoretic separation of the clay and that such change as the clay finally underwent was due to the preliminary deflocculation and settling. At the present time Bleininger[23] is of the opinion that, although the " osmose " process can be made to work satisfactorily, the same results can be obtained without the use of the electric current by deflocculating the clay with caustic soda, thus removing the granular impurities, coagulating the suspension with acids or aluminum chloride and filtering out the precipitated material. At any rate no electro-osmose plants are in operation in the United States, while the precipitation process is giving satisfaction at the Saylersburg, Pa. plant of the Miner-Edgar Company, Brooklyn, N.Y., and that of the Georgia Kaolin Co., at Macon, Georgia.

There seems to be a great deal of misunderstanding with regard to the extent to which the " osmose " machine acts as a purifier. Ormandy points out that clay or kaolin particles are electro-negative, silica is more or less neutral, while oxides of iron and titanium are positive. Hence only kaolin migrates to the anode, silica settles out and the iron collects at the cathode. In the first place, suspended ferric oxide, although called a positive colloid, is not necessarily positive against an alkaline solution and probably is electro-negative[24] unless there happens to be present in the solution some strongly adsorbed cation, such as calcium or magnesium, to counteract the effects of hydroxyl. Another point which has been overlooked is the condition of the iron oxide in the clay—if the oxide is adsorbed by the kaolin the electrical treatment cannot remove an appreciable amount of iron from the clay. To be sure, Schwerin[25] claims that adsorption compounds can be broken up by electrical endosmose or cataphoresis, but this can occur only when there is a relatively large amount of one substance in the liquid phase *and in adsorption equilibrium with the solid phase.* As to the results actually obtained, it is interesting to note that of 25 clays reported

[21] Cf. Brit. Pat. 3434 (1913).

[22] *Trans. Am. Cer. Soc.* **15**, 338 (1913); *Techn. Paper U.S. Bur. Standards* **51**, (1915).

[23] Private communication to the author, June, 1918.

[24] Ferric oxide peptized by glycerine and NaOH is negative and migrates to the anode. Fischer and Kusnitzky: *Biochem Zeit.*, **27**. 311 (1910).

[25] Brit. Pats. 14369 (1912).

by Ormandy, 15 contained less iron after purification while 8 contained more.

Shortly before the war, Schwerin organised the Elektro-osmose Aktien Gesellschaft of Frankfort-on-the-Main, for the purpose of developing his multiplicity of inventions, commencing operations with a capital of three million marks.[26] Several improvements and changes have been made in the clay process since that time, along the lines of adding negative colloids (silica, humus) to the clay suspension,[27] employing electro-osmotic pressure filters,[28] using diaphragms[29] differing (1) in size of pores, (2) in sign and intensity of interface potential, and making several changes in the "osmose" machine itself. There is not enough available information for one at the present time to evaluate those modifications. The process as a whole appears to be far the most promising one Schwerin has developed.

Electrical Tanning.

Electrical tanning[30] of leather is the oldest practical application of electrical endosmose, having been originated, according to Buse, by Grosse in 1849. In 1874 de Meritens, at Petrograd, used electricity in 600 tan pits, employing a layer of carbon at the bottom as anode, placing on this alternate layers of hides and tan bark and concluding with a sheet of zinc as cathode. Buse describes other systems (Groth, Worms and Balé, etc.) and reports that the electric current increased the rate at which tannin was taken up from 338 to 533.

So far as one is able to judge, electricity has been applied to tanning processes for two purposes, (1) to hasten the process by heating the bath electrically, (2) to hasten the process electro-osmotically by the tan liquor into and through the skins. For the first purpose either direct or alternating current may be used, but for the latter only direct current can be employed. It seems incorrect to advocate as Williams does the use of an alternating current to produce the endosmotic effect of a direct current without at the same time causing electrolytic decomposition of the tannins.

The electro-osmotic method of tanning is decidedly more rapid than the ordinary diffusion process and would be a distinct success were it not for anodic oxidation of the tannin. Schwerin[31] has endeavoured to prevent this by surrounding the electrodes with diaphragms, but his process and apparatus appear to be excessively intricate. It ought, however, to be possible to solve all these difficulties, for it is undoubtedly in this field and in impregnation in general that electrical endosmose should find widest and most successful application.

[26] *Elektrotechn. Zeit.*, **35**, 860 (1914).
[27] Brit. Pats. 27931 (1911), etc.
[28] Brit. Pats. 23545 (1912).
[29] Brit. Pats. 2466 (1912).
[30] Folsing: *Zeit. Elektrochemie*, **2**, 167 (1893); Rideal and Trotter: *Jour. Soc. Chem. Ind.*, **10**, 425 (1891); Buse: *Ibid.*, **19**, 57 (1900); Rideal and Evans: *Ibid.*, **32**, 633 (1913); Williams: *Jour. Am. Leather. Chemists. Assoc.*, **8**, 328 (1913); Groth: Brit. Pat. 19239 (1912).
[31] Brit. Pat. 21190 (1914).

Preservation of Timber. Electro-osmotic Impregnation.

At various times it has been proposed to dry timber by electro-osmotically removing the sap. While electrical endosmose can scarcely prove suitable for this process alone it might be very effective in replacing the sap juices with liquid disinfectants. Alcock and Company, Proprietary, Ltd.,[31A] of Melbourne, propose to impregnate timbers electrically, by placing them on end in a shallow cathode vessel containing a conducting liquid and driving into the upper ends hollow metal anodes filled with the liquid preserving medium with which the wood is to be impregnated. On passing a current, electrical endosmose to the cathode takes place, sap is forced out of the timber and into the lower receptacle and its place is taken by the liquid preservative forced in at the top. If the consumption of electric power is not too great, the method ought to prove a success. In this connection it is interesting to find a note[32] to the effect that the injury to trees caused by stray currents may be due to electrical endosmose. This is quite possibly true in case the electric current is a direct one.

Manufacture of Bricks. Lubricating Metal Surfaces in Contact with Clay.

A very effective and apparently mysterious process which is unquestionably an application of electrical endosmose was announced by Dawkins[33] in 1913, at the Chicago Convention of the National Brick Manufacturers Association. Wet clay has a distinct tendency to adhere to smooth metal surfaces. To prevent this a lubricant is used, the lubricants including oils, emulsions and water itself. Water is particularly useful because a layer of it on the metal prevents the clay from sticking, softens the surface of the clay as it is being cut or moulded and gives the brick a smooth finish. It was found that if metal in contact with the clay is made cathode and a current is passed, the clay no longer tends to adhere and all the effects of lubrication are duplicated. In making wire cut bricks electrical "lubrication" is said to reduce the power consumption by 25 to 30 per cent.

It has been suggested that the current forms a layer of hydrogen over the electrode and that this causes the apparent lubrication. What really happens is this: when the current flows water is carried through the clay to the cathode (the metal) and forms a layer between it and the clay; it is this layer of water which prevents the clay from sticking and acts as a lubricant.

ELECTRO-THERAPEUTICS. ELECTRO-OSMOTIC INFILTRATION OF DRUGS.[34]

Shortly after the early experiments, especially those of Wiedemann, had demonstrated the ease with which electrical endosmose

[31a] Brit. Pat. 25175 (1910).
[32] Schneckenberg: *Elektrochem. Zeit.*, **19**, 151; Chem Abstr.
[33] Clayworker 57, 426 (1912) Cf. Brit. Clayworker: **22**. 91, 92 (1913).
[34] Morton: *Cataphoresis* (1898); Herdman: Bigelow's *Internat. Sys. of Therapeutics*, **30** (1894); Peterson: *Ibid.* C 1 (1894); Jones: *Med. Electricity* (4th Ed.) 230 (1904); Traube and Berczeller: *Internat. Zeit. Biol.* **2**, 107 (1915).

occurs through animal membranes, attempts were made to apply the process to living membranes and tissues. In 1859 Richardson produced what he termed " voltaic narcotism " or local anæsthesia produced electrically by forcing morphine through the skin and into the tissues of the subject. The process appears to have been a combination of electrolysis and electrical endosmose. Since Richardson's time a great deal of interesting work has been done on the subject and it has been quite conclusively demonstrated[35] that liquids bearing narcotics and drugs of all kinds can be forced by the electric current into and through living skin and tissue. Electrical endosmose has been applied in dentistry as well, in the local anæsthesia[36] of sensitive dentine and in bleaching teeth with hydrogen peroxide.[37] Electric transference of ions in solution complicates most of these so-called " cataphoretic " experiments (such as Edison's[38] on the infiltration of lithium chloride) as Leduc has shown.[39]

Miscellaneous.

Schwerin has patented an electro-osmotic process[40] of extracting sugar from beet. Sliced beet roots were placed between pervious walls and electrolyzed. The sugar solution containing the soluble albumenoids was driven through the cathode diaphragm and in this manner the beets were extracted. By placing water between the anode and the anode diaphragm the soluble acids in the beets were said to be removed by electrolysis and collected—an improvement which prevented the sugar from inverting. The process appears to have been electrically accelerated dialysis, except in so far as the acidic impurities were more or less segregated. In more recent years Schwerin through the Elektro-osmose A.G. has been granted a large number of patents dealing with the purification of colloidal and non-colloidal mixtures and the resolving of such mixtures into their constituents. By using diaphragms impervious to the colloid but pervious to dissolved ions, the latter may be driven out by electrolysis and collected about the electrodes which are usually surrounded in the beginning by pure water. A simple example is the case of extracting sugar and acids from beets, which we have just mentioned. Suspended colloids may themselves be fractionated by using diaphragms (1) the pores of which vary in size (Cf. ultrafiltration) (2) the interface potentials of which are different. When the diaphragm operates because of differences in permeability (size of pores) one is dealing with ultrafiltration accelerated by electrical endosmose. In the other case negative diaphragms are said to hold back positive colloids or vice versa and here th process is analogous to the mutual precipitation of electrical suspensions. It is doubtful, however, whether really satisfactory separations can be made by this

[35] Cf. Barratt and Harris : *Biochem. Jour.*, **6**, 315 (1912) ; Morton : *Cataphoresis* 89 (1898).

[36] Morgenstern : *Elecvrochem. Zeit.*, **15**, 189, 214, 240 ; *Cf. Chem. Abstr.* **3**, 1203 (1909).

[37] Morton : *Cataphoresis*, 41 (1898).

[38] Peterson : *Bigelow's Internat. Sys. of Therapeutics* C13 (1894).

[39] Jones : *Med. Electricity* (4th Ed.) 228 (1904).

[40] Brit. Pat. 8068 (1901) ; 14195 (1903).

second method because the adsorption of the suspended colloid may change the sign of the diaphragm. Schwerin claims to apply the method in the production of pure colloidal silica,[41] in the tanning of leather, in the purification of gelatine (glue)[42] dyes,[43] metal sols[44] and alumina[45] and in the treatment of serum.

Summary.

In this report there have been described applications of electrical endosmose or of electrical endosmose and cataphoresis in the processes of dewatering peat and other substances; treatment of clay; tanning; filtration; medicine; separation of colloidal and non-colloidal mixtures; and so forth. No mention has been made of certain processes, such as electrical treatment of emulsions and the use of addition agents in electro-plating, which are clearly instances of applied cataphoresis and are so recognized.

British Patents. Electro-osmotic Processes.

In the case of Patents dated as of the years 1900 to 1913 inclusive the original Specifications have been consulted. The information contained in the more recent patents has been obtained from Chemical Abstracts and other sources.

1900.

12431, July 10. B. Schwerin, Munich. "Improvements relating to the extraction of water or other liquid from mineral, vegetable and other substances." Evidently first British patent. Discusses electrical endosmose, the utilisation of the "motorial" action of the electric current in removing water from peat and describes apparatus for so doing.

1901.

8086, April 19. B. Schwerin, Munich. "Improvements relating to the extraction of sugar. Sliced beet-roots placed between pervious walls and submitted to electro-osmose and electrolysis. Sugar, soluble albumin and water driven to cathode. Places water between solid material and anode; the acids in the beets collect by electrolysis in the anode liquid and are prevented from inverting sugar. Describes apparatus.

22301, November 5. B. Schwerin, Berlin. Cf. 12431 (1900). Describes apparatus for dewatering peat.

1903.

1717, Jan. 23. J. Doull. Use of electric current in drying materials.

14195, June 25. C. D. Abel, for Siemens and Halske A. G., Berlin. Elaborate discussion of electrical endosmose and

[41] Brit. Pat. 9237 (1914).
[42] Brit. Pats. 21448, 21483 (1914).
[43] Brit. Pats. 9565, 9566 (1915).
[44] Brit Pat. 9261 (1914).
[45] Brit. Pats. 6727, 7212 (1915).

cataphoresis. Use of diaphragm aids in removing water from peat. Interesting to note that water passes to *anode* when current is passed through a porous cup containing iron "oxychloride" (colloidal ferric hydroxide) and the "oxychloride" is reduced to a jelly (dewatering of colloidal suspension with subsequent formation of an iron oxide jelly). Purification of "saccharine juices."

1904.

126, Jan. 4. B. Kittler, Memel, Germany. Apparatus (continuous) for dewatering peat.

3795, Feb. 16. Imray for Farbwerke, vorm. Meister, Lucius u. Brüning Höchst, a/M. Dewatering peat. Heats apparatus and material. Cf. 12431 (1900).

24670, Nov. 14. Imray for Farbwerke, vorm. Meister, Lucius u. Brüning Höchst, a/M. Dewatering peat. Ingenious apparatus for continuous operation, consisting of two endless belt conveyers, one of which may be an electrode.

1905.

4792, March 8. W. Simm. Dewatering peat. Doubtful if Simm really uses electrical endosmose at all as he specifies alternating current. Mentions heating effect of the current.

1907.

2226, Jan. 29. J. C. Verey and L. Downes. Electric-osmotic apparatus for dewatering peat.

10024, Apl. 30. Farbwerke, vorm. Meister, Lucius u. Brüning, Höchst a/M. Depositing suspended articles on electrodes by cataphoresis. Fractional cataphoresis, with especial emphasis on purifying and dewatering clay. Better results are obtained by causing fresh suspension to enter cell by passing close to a cathode of large surface. In this way the suspension passes through a diluted region and settling out of impurities is facilitated.

1909

10793, May 6. B. Schwerin. Production of electric current by Quincke's method (diaphragm currents). Claim is made of the use of suitable electrolytes to increase effectiveness of process. Importance of making certain that diaphragm and liquid are in equilibrium. "Action of electrolytes is so great, it seems generation of current is dependent upon presence of ions." With diaphragms of quartz, an alkaline liquid (pyridine and water), pumped through under pressure gave the following results:

Pressure.	Volts.	Amperes.	Watts.
10	4	0·01	0·04
20	8	0·02	0·16
40	16	0·04	0·64
80	32	0·08	2·56

The efficiency was calculated from the formula:

$$\text{Efficiency} = \frac{\text{volts} \times \text{amperes}}{\text{pressure} \times \text{discharge of water}}$$

It was found experimentally that the efficiency remained the same for each of the above pressures but increased as the pores in the diaphragm became finer because the discharge of water at constant pressure was thereby lessened.

1910.

132, Jan. 3. F. Arledter, Hamburg. Electric sizing of paper (cataphoresis?).

25175, Oct. 29. Alcock and Co. Proprietary Ltd., Melbourne. Drying timber by electrical endosmose. Stand timber on end in shallow vessel as cathode containing a small quantity of conducting liquid and connect top of timber with suitable anode. Sap is driven endosmotically out of timber into lower vessel, following which solutions of resin, sugar or creosote may be driven in from above and the timber impregnated with preservative.

1911.

3364, Feb. 9. B. Schwerin. Accelerates process of electro-osmose (cataphoresis) by adding *acids* (acetic acid, CO_2, etc., to those substances which migrate to cathode and *bases* ($NaOH$, NH_4OH) to those substances which migrate to anode. Hastens draining of peat by adding a little alkali to the pulp. An interesting application of Perrin's rule. In 2379 (1911) Schwerin patents use of *acids* to peptise substances (elutriate) which wander to cathode and *bases* to peptise substances which wander to anode.

11626, May 13. B. Schwerin. Adding electrolytes, especially NA_2SO_4 to peat. Data on improvement which results are not particularly convincing.

17597, Aug. 2. Felten and Guilleaume Carlswerk A.G., Carlswerk. Claim use of non-aqueous solvents in electro-osmotic (cataphoresis) separations. Separation of dyes in alcohol, etc.

27931, Dec. 12. B. Schwerin. In 3364 (1911) use of electrolytes has been claimed. In order to cause deposits at electrodes to adhere more firmly to latter add electro-positive or electro-negative [adsorbed] colloids. For example, peptises clay with a little sodium silicate, allows coarse particles to settle out and electrolyzes. With 100 volts and 1·6 amps. obtains 140 g., containing 65 per cent. clay, in 5 minutes. Clay adsorbs electro-negative colloidal silicic acid from water glass and is carried to the anode.

28185, Dec. 14. Gesellschaft für Elektro-osmose (Schwerin). Frankfurt a/M. Dewatering and purifying clay. Deflocculates clay with dilute NaOH, allows thin slip so made to settle in vats, and finally treats in "electro-osmose" machine. Electrolyte added supposed to peptize clay and coagulate impurities.

1912.

725, Jan. 9. Gsellschaft für Elektro-osmose. Frankfurt a/M. Apparatus (osmose machine) for purifying and dewatering clay. Rotating cylinder anode and wire gauze cathode. Cir-

culating device to prevent impoverishment of suspension between anode and cathode.

10370, May 1. J. E. Jameson and O. H. Valpy, London. Electric current passed into peat at 100° C. and under pressure (10 Atm.). Current may be "continuous or alternating" (*sic*), and "decomposes hydrocellulose." It is possible that the alternating current in some manner breaks down the jelly of peaty material.

14235, June 18. B. Schwerin. Use of electro-osmose in connection with manufacture of refractory articles, baked without binder.

14369, June 19. B. Schwerin. Separates mixtures of different substances in suspension by fractional cataphoresis. Also separates by means of diaphragms of different permeability; Apparatus really a kind of electric "ultrafilter."

19239, Aug. 22. L. A. Groth, London. Electric tanning. Details of apparatus.

23545, Oct. 15. Gesellschaft für Elektro-osmose (Schwerin). Drying peat, clay, kaolin, etc., by pressure combined with electro-osmose Electro-osmotic filtration. Pressure may be reduced from 20 atmospheres to 1 atmosphere by combining electro-osmose (cataphoresis) with it. The higher the voltage used the more rapid the filtration. Apparatus.

24666, Oct. 28. B. Schwerin. Use of electrically-charged diaphragms in the fractional separation of suspended colloids. depending upon

1. Difference in size of pores.
2. Differences in interface potentials.

Electro-negative diaphragms tend to hold back electro-positive colloids and vice versa.

29826, Dec. 27. Gesellschaft für Elektro-osmose and H. Illig. Improved apparatus for dewatering and purifying clay. Cf. 725 (1912).

1913.

3434, Feb. 10. Gesellschaft für Elektro-osmose (Schwerin). Making ceramic articles without adding flux to cause sintering at temperatures below melting point. No flux (steatite, magnesium silicates) necessary with clay purified by electro-osmose, owing to the extreme fineness of the particles. In one case a clay treated by the osmose process sintered at a temperature more that 300° C. below its melting point, and did this without the addition of a flux.

6668, Mar. 18. A.L.C. Nodon, Bordeaux. Electrical preservation of railway sleepers (ties). Uses alternating current (?) and 1 per cent. $ZnCl_2$ solution.

10873, May 8. Gesellschaft für Elektro-osmose (Schwerin). Cf. 23545 (1912) Electro-osmotic filter with electrodes of hard lead.

26061, July 21. Gesellschaft für Elektro-osmose (Schwerin). Further mechanical improvements in osmose machine for clay.

1914.

6993, Mar. 19. *Elektro-osmose Akt. Gesellschaft* (*Schwerin*). Facilitates dewatering of peat by previously subdividing material in a ball mill and adding electrolyte such as NaOH to increase the rate of cataphoresis and endosmose.

6995, Mar. 19. *Elektro-osmose Akt. Gesellschaft* (*Schwerin*). Cf. 6993 (1914). Adds adsorbed colloid before grinding peat. Colloidal silicic acid or humic acids are suitable. By adding sodium silicate obtains both a suitable electrolyte (NaOH) and colloidal silica. Adsorbed colloid peptizes the solid and being strongly electro-negative in dilute NaOH hastens the migration to the anode.

9237, Apr. 14. *Gesellschaft für Elektro-osmose* (*Schwerin*). Electro-osmotic preparation and purification of colloidal silicic acid. Places 5 to 10 per cent. sodium silicate solution between two porous diaphragms—one around cathode and the other around anode. By using a *neutral* diaphragm (composed of carborundum plus alundum) about the cathode, the alkali is electrolyzed out of the sodium silicate, and no silica is carried into the cathode compartment, since no electrical endosmose takes place through the cathode diaphragm. With parchment above anode, no colloidal silica can get into anode compartment but soluble acids can do so. Obtained colloidal solution of silica in the middle compartment. Platinum or lead-antimony anodes; brass gauze cathodes. Typical "electro-osmotic" multiple diaphragm process. Cf. German Pat. 283,886, Apr. 15, 1913.

9261, Apr. 14. *Gesellschaft für Elektro-osmose* (*Schwerin*). Making stable metal sols by using colloidal silicic acid as protecting agent, reducing metal salt with hydrazine hydrate and purifying subsequently by process such as specified in 9237.

11823, May 13. *Gesellschaft für Elektro-osmose* (*Schwerin*). Separating colloids, etc., by electrical endosmose and cataphoresis.

19849, Sept. 16. *Gesellschaft für Elektro-osmose* (*Schwerin*). Tanning and dyeing by electro-osmose. Places leather or adsorbing substance, together with tannin solution in compartment between two or more diaphragms, impervious to tannin but pervious to dissolved electrolytes. Claims simultaneous purification of tannin solution by electrolysis and impregnation of leather.

21189, Oct. 19. *Gesellschaft für Elektro-osmose* (*Schwerin*). Changes interface potential of diaphragms by addition agents. Thus Cr_2O_3, makes a leather diaphragm more positive (leather adsorbs Cr_2O_3 which is distinctly electro-positive). Methylene blue (basic dye) makes viscose positive (viscose adsorbs the dye cation). Adsorbed acid dyes make diaphragms electro-negative. Interesting patent based on selective ion adsorption or on the adsorption of charged colloids.

21190, Oct. 19. *Gesellschaft für Elektro-osmose* (*Schwerin*). Modifies 19849 to allow preliminary purification of tan liquor.

Uses three diaphragms instead of two and places tan liquor next the hides in a separate compartment between the hides and the cathode. Anode, cathode and hides are immersed in water. On passing current acid and basic impurities in the tan liquor are electrolyzed out and carried into the anode and cathode compartments, after which tannin is said to migrate into compartment containing hides. Process seems hopelessly complicated and not at all practical. Theory of process not very clear.

21448, Oct. 23. B. Schwerin. Gelatin or glue placed between diaphragms impervious to glutin and electrolyzed a cell containing anode, cathode and gelatin compartments. Soluble electrolytes removed and albumins precipitated. Other complicated modifications are described. Combined electrical dialysis and ultrafiltration process.

21483, Oct. 24. Gesellschaft für Elektro-osmose (Schwerin). Cf. 21448 (1914). Uses hide or leather waste between diaphragms instead of glue.

1915–1916.

6727, May 5. Elektro-osmose Akt. Gesellschaft (Schwerin). Electrical purification of alumins. Cf. 21448 (1914).

7212, May 13. Elektro-osmose Akt. Gesellschaft (Schwerin). Cf. 6727. Electrical purification of alumina.

7590, May 20. Elektro-osmose Akt. Gesellschaft (Schwerin). Use of centrifuge to hasten preliminary settling process in the "electro-osmotic" purification of clay.

9565, 9566, June 30. Elektro-osmose Akt. Gesellschaft (Schwerin). Electrical purification of dyes. Dye suspension placed in inner compartment and shielded from oxidizing and reducing action of electrodes by means of diaphragms impervious to dyes. Cf. 21448 (1914).

11659, Aug. 12. Elektro-osmose Akt. Gesellschaft (Schwerin). Treatment of clay.

COLLOID-CHEMISTRY IN THE TEXTILE INDUSTRIES:

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Introduction.

Although a considerable amount of research work has been done on the chemistry of textile fibres, particularly cotton, no definite information has been obtained on the chemical constitution of the substances composing them. The colloidal nature of these substances always stands in the way of pure chemical research. There are many processes used in the textile industry where a knowledge of the chemical constitution of the substances composing fibres is unnecessary, the changes produced being more physical than chemical. Chemists are naturally attracted by the idea that all the physical properties of a substance are dependent on the chemical constitution of its molecules, but the properties of colloidal barium

sulphate are quite different from those of the crystalline substance although the chemical constitution is considered to be the same in the two cases. The suggestion has been made[1] that colloidal barium sulphate consists of extremely minute crystals, but this does not explain the difference in physical state. The chemist's idea can only be upheld by a considerable modification in the conception of molecules as present in solid substances. The Braggs[2] have established beyond doubt that the fundamental units of a crystal are atoms, not molecules. Many chemists[3]—[8] have cast doubt on the crystal models of the Braggs', except that of the diamond, simply because they are against the generally accepted ideas on valency. It has been suggested[9] that one of the interesting problems of the future will be to reconcile the X-ray crystal models with the molecular hypothesis. Since the X-ray models have been deduced from positive evidence whereas no positive evidence has ever obtained in favour of the molecular hypothesis as applied to solids, the author considers that it is the molecular hypothesis which requires broadening. The original definition of a molecule was the smallest particle of a substance which could exist; with the discovery of chemical polymerisation this definition has been narrowed somewhat. The author considers that the difficulty of reconciling the X-ray models with the molecular hypothesis disappears if one admits a crystal to be a polymeride or single molecule as suggested by Langmuir.[13] This idea has far reaching consequences of very great importance in colloid chemistry, since the necessity for admitting a high molecular weight as a special characteristic of colloids disappears. A single crystal may be considered as a single molecule since it consists of atoms bound together by the same forces which bind together the atoms in the simple molecules found in gases. The molecular weight of the crystal is then proportional to its size. This view is entirely in agreement with the observations in brownian movement of particles in different degrees of dispersion which were shown by Perrin[10] to be explained by the kinetic theory of gases. There are numerous other consequences of the idea of considering crystals as polymerides which it is not intended to discuss here.

Regarding the chemical nature of fibres, chemists have divided opinions, some considering them to be very complex bodies of high molecular weight, others to be physical forms of insoluble substances of possibly low molecular weight. These opinions may be taken to be identical in the light of the idea discussed above.

In the case of vegetable fibres, the suggstion has recently been made[11] that the fibre substances, celluloses, are liquid systems; this brings forward the question of reconsidering the definitions of liquid and solids. At present, these are somewhat rigid and bodies possessing properties of both states of matter are considered to be mixtures. The author does not hold this view, but considers that there is no distinct line of demarcation between the solid and liquid states any more than there is between colloidal—and true—solution. The semi-solid state of many colloids does not necessarily imply the presence of both solid and liquid phases. It is, therefore, still an open question whether the celluloses are mono—or diphasic systems.

The fibres possess many physical properties in common with other colloids such as indiarubber and gelatine.

When subjected to stress in a dry condition they become deformed and acquire increased double refraction which persists when the stress is removed.[12] This increased double refraction shows the presence of extra internal stresses resulting from the deformation. When placed in a solvent which tends to produce swelling—water in the case of fibres—these extra internal stresses disappear and the fibres regain their original shape. When compressed under boiling water most fibres become permanently deformed, no internal stresses being produced.

These theoretical points have an important bearing on many of the phenomena met with in the treatment of textile materials.

(A) *Introduction.*

[1] Von Weimarn, *Grundzuge der Dispersoid chemie*, Leipzig (1912).
[2] W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc.* **A. 87**, 277 (1914), etc. See also *Trans. Chem. Soc.*, p. 252 (1916).
[3] A. Smits and F. E. C. Scheffer, *Proc. K. Akad. Wetlensch*, Amsterdam, **19**, 432 (1916).
[4] A. Fock, *Centr. Min.* 392 (1916).
[5] J. Beckenkamp, *ibid.* 97 (1917).
[6] J. Stark, *Jahr. Radioaktiv. Electonik*, **12**, 280 (1915).
[7] F. Rinne, *Zeit. anorg. Chem.*, **96**, 317 (1916).
[8] P. Pfeiffer *ibid.*, **92**, 376 (1915); **97**, 161 (1916).
[9] H. M. Dawson, *Annual Report Chem. Soc. (Physical Chemistry)* (1917).
[10] J. Perrin, *Brownian Movement and Molecular Reality.*
[11] C. F. Cross, *Presidential Address to Soc. Dyers and Colourists*, **34**, 19 (1918).
[12] W. Harrison, *Proc. Roy. Soc.* **A. 94**, 460 (1918).
[13] I. Langmuir, *Journ. Amer. Chem. Soc.*, **28**, 2221 (1916).
[14] Tinker, *Proc. Roy. Soc.* **A. 92**, 357 (1916).
[15] W. Moeller, *Koll. Zeit.* **19**, 205, 213 (1916); **20**, 242, 257 (1917); **23**, 11 (1918).
[16] J. R. Katz, *Koll. Ch, Beith.*, **9**, 1 (1917).
[17] Bachmann, *Koll. Zeit*, **9**, 312 (1911); **11**, 150 (1912); **12**, 204 (1913); **23**, 85 (1918); also *Zeit. anorg. Chem.*, **73**, 125–172 (1911); **79**, 202 (1912); **100**, 76 (1917).
[18] Debye & Scherrer, *Phys. Zeit.*, **18**, 291 (1917).

Cotton.

Regarding the chemical constitution of the substance of the cotton fibre, six formulæ have already been proposed, but none of these have been established. (Refs. [10–16]).

Cross originally held that the cellulose molecole was large, being composed of units of a certain type bound together; Green favoured a simple formula. In a recent address (Ref. A.[11]) Cross stated that there are no grounds for the assumption of large molecules in the strict chemical sense. He considers that the celluloses are liquid systems capable of large volume changes and also solution aggregates of amphoteric character. He suggests that the units in the cellulose aggregate may have dimensions less than C_7. One difficulty in the way of the acceptance of a very simple formula for cellulose is the number of hydroxyl groups which chemical methods prove to be present; all the bodies of the same chemical composition, known up to the dimensions C_7, having a corresponding number of hydroxyl groups are soluble in water.

It is quite likely that the units in the cellulose aggregate are bound together in a similar manner to the units in a crystal, although

perhaps not in a regular formation. As already suggested, there is no necessity to discuss the molecular weight of the cellulose colloid since it only exists in the solid state. The fibre itself may be considered to be a molecule in so far as the atoms composing it are bound together in the same way as in any other molecule.

Mechanical disintegration produces changes corresponding to depolymerisation, B [25] [26] [31] [34] [35] in the same way that mastication is considered to produce depolymerisation of rubber. (Compare *Journ. Soc. Chem. Ind.*, **37**, 313A (1918).)

The substance of the cotton fibre is known in many colloidal states; in the fibre itself it exists as a porous, adherent mass, showing turbidity in the ultramicroscope, which indicates amicroscopic structure. Treatment with sulphuric acid of 1·70 Sp. G causes the fibre to swell and eventually pass into solution. In the swollen state the fibre shows a distinct granular structure, which the author succeeded in photographing.[22–23] Since the acid acts in the direction of solution and not coagulation, the author is of the opinion that the structure of the swollen fibre is an extension of that of the original fibre, this extension allowing the structure to be resolved.

The double refraction of cotton fibres has been shown to be due to the presence of internal stresses, which become active when the fibre is softened.[22–23] There is no doubt that the cellulose is in different colloidal states in different parts of the cotton fibre, the outer portions being more solid than the inner. There are markings on the fibre (Refs. [9–19]) which have physiological importance which it is not proposed to discuss in this review. The colloidal chemical investigation of cotton indicates that it is first formed in somewhat gelatinous filaments which harden from the outside by drying or by some chemical change.

The following extract from W. L. Ball's observations on the development of cotton appear to be in agreement with the view just expressed:—

"The full diameter of the seed hair is attained almost at once, when its length is only $\frac{1}{10}$ m.m. while its length continues to increase until the 25th day of development after which its wall begins to thicken, giving strength to the lint. This thickening is not uniform, but leaves simple pits in the wall set obliquely, and the closure of these pits when the wall dries after the boll opens, gives twist to the fibre. The uninucleate cell contents remain alive until the boll begins to open, when they die from desiccation.

"The cell wall is extremely thin for the first three weeks and the cuticle which covers it can scarcely be differentiated unless the wall has been swollen with Schweitzer's reagent when (being unaffected by the ammoniacal copper oxide) it causes the familiar beaded appearance, the cellulose of the wall swelling through the torn places in the cuticle."

The difference between the outer cell wall or cuticle and the inner portions of the fibre is most probably one of colloidal state[23] and not of chemical nature. A similar difference exists between the outer layers of starch granules and the inner portions and it has been shown that this difference is one of colloidal state.

The colloidal state of cellulose is modified in the direction of distension by treatment with strong alkalies, caustic soda, caustic potash tetramethyl-ammonium-hydroxide and by several other substances. A still greater degree of swelling is produced when cotton is overworked in the hollander used in the paper-making industry.[25] [26] The maximum degree of dispersion is attained when the cotton is treated with cellulose solvents.

It has been observed that freshly precipitated cellulose is soluble in caustic soda but that this solubility disappears when the cellulose is dried. A similar change is produced when precipitated starch is dried. These changes are the common result of gel-dehydration.

Iodine forms a useful reagent in conjunction with hydrating agents such as potassium codide, zinc chloride and sulphuric acid, for indicating the different colloidal states of cellulose. The strength of hydrating agent required to give the blue colour indicates the degree of dispersion of the cellulose. It is interesting to note that starch celluloses can be prepared which give the blue colour with iodine under the same conditions as cellulose.[22] This does not necessarily imply that there is any chemical relationship between starch and cellulose since the blue colour has been shown to be due to colloidal iodine and numerous substances have been found which give the reaction.

(B). *Cotton:*

Books of Reference.

[1] Cross & Bevan, *Cellulose and Researches.*
[2] Schwalbe, *Die Cellulose.*
[3] Worden, *Nitrocellulose Industry.*
[4] O. N. Witt, *Chem. Tech. der Gespinnst-fasern Braunschweig*, (1888).
[5] Monie, *The Cotton Fibre, London*, (1890).
[6] Bowman, *The Structure of the Cotton Fibre.*
[7] H. Kuhn, *Die Baumwolle.*
[8] Flatters, *The Cotton Plant*, (1906).
[9] W. L. Balls, *The Development and Properties of Raw Cotton*, (1915).

References.

[10] Tollens, *Handbuch der Kohlehydrate* II., 252, (1895).
[11] Vignon, *Bull. Soc. Chem.*, **21**, 599, (1899).
[12] Bernadou, (Compare (2), p. 349).
[13] Cross & Bevan, *Trans. Chem. Soc.*, **79**, 366, (1901).
[14] A. G. Green, *Journ. Soc. Dyers & Cols.*, **20**, 117, (1904).
[15] Cross & Bevan, *Ibid.*, **32**, 135, (1916).
[16] A. E. Sunderland, *Ibid.*, **32**, 230, (1916).
[17] Crum, *Trans. Chem. Soc*, **1**, 409.
[18] Muller Jacobs, *Journ. Soc. Dyers & Cols.*, **11**, 95, (1885).
[19] H. De Mosenthal, *Journ. Soc. Chem. Ind.*, **23**, 292, (1904); **26**, 443, (1907).
[20] Haller, *Zeit. für Farben u. Textil Chem.*, **8**, 125, (1907).
[21] Herzog, *Koll Zeit.*, **5**, 246, (1909).
[22] W. Harrison, *Journ. Soc. Dyers & Cols.*, **31**, 198, (1915).
[23] W. Harrison, *Trans. Nat. Assoc. Cotton Manfrs.*, **101**, 201, (1916).
[24] Haller (Structure of Cotton), *Koll. Zeit.*, **20**, 127, (1917).
[25] Cross, *Papier Zeitung*, **33**, 3246, (1908).
[26] Briggs, *Papier Fabrikant*, **5**, 2644, (1907); 46, (1910).
[27] Fenton (Action of hydrochloric acid), *Trans. Chem. Soc.*, **73**, 554, (1898): **75**. 427, (1899); **79**, 361, 807, (1901); **99**, 1193, (1911).
[28] Erdmann & Schaeffer, *Ber.*, **43**, 2398, (1910). (Dry distillation of cellulose).
[29] Pictet and Sarasin, *Comp. Rend.*, **166**, 28, (1918). (Dry distillation of cellulose and starch).
[30] Sarasin, *Arch. Sci. phys. Nat.* (1918), pp. 5–32.
[31] Fort, *Journ. Soc. Dyers & Cols.*, **34**, 9, (1918).

[32] S. Judd Lewis, *Ibid.* **34**, 167, (1918).
[33] W. L. Balls, *Journ. Soc. Arts.*, p. 389, (1918).
[34] C. F. Cross, *Journ. Soc. Dyers & Cols.*, **34**, 215, 247, (1918).
[35] W. Harrison, *Ibid.* **34**, 218, (1918).
[36] Knecht & Hall, *Ibid.* **34**, 220, (1918).

Compound Celluloses:

[37] Cross & Bevan, *Cellulose*, pp. 89–232.
[38] Schwalbe, *Die Cellulose*, pp. 366–483.
[39] Stocks, *First Report on Colloid Chemistry*, pp. 58–64.

Animal Celluloses:

[40] Worden, *Nitrocellulose Industry*, p. 1.
[41] Irvine, *Trans. Chem. Soc.*, 95, 564, (1909).

Cellulose Solutions.

The so-called solutions of cellulose are really colloidal solutions. The best known solvents are Schweitzer's reagent,[6 18 21] zinc chloride solution and sulphuric acid. Numerous other solvents have been found in recent years.[7] Recently,[8] it has been stated that cellulose can be dissolved in solutions of most salts when heated under pressure.

Regarding the solution of cellulose in ammoniacal copper solution Cramer[9] came to the conclusion from osmotic measurements that it was a true solution. Erdmann,[10] on the other hand, considered it to be a very highly hydrated gel. Cross & Bevan[11] expressed the view that the copper compound combined with the cellulose to form a colloid double salt.[19–20] The dialysis of these copper solutions has been studied by Grumaux[12] who came to the conclusion that it was the non-dialysable portion of the solution of copper hydrate in ammonia which acted as a solvent for cellulose.

It is important to note that cuprammonium hydroxide is not so strong an alkali as caustic soda.[13]

The solution of cellulose in ammoniacal copper solution has been stated to be optically active[14–15] a view which does not appear to be substantiated.[16] The solution of cellulose in hydrochloric acid is optically inactive.[17]

(C) *Cellulose Solutions.*

[1] Compare B.[1]
[2] Compare B.[2]
[3] Compare B.[3]
[4] Czapek, *Biochemie der Pflanzen*, Jena, 1905.
[5] Abderhalden, *Biochem Handlexikon*, Berlin, 1911 (II) Cellulose.
[6] Schweitzer, *Journ. für prakt. Chem.*, **72**, 109, 3441 (1857).
[7] Deming, *Journ. Amer. Chem. Soc.*, **33**, 1515 (1911).
[8] Weimarn, *Koll. Zeit.*, **11**, 41 (1912).
[9] Cramer, *Journ. für prakt. Chem.*, **73**, 1 (1858).
[10] Erdmann (Compare B[1], p. 11).
[11] Cross & Bevan, Textbook of Papermaking, p. 8.
[12] Grumaux, *Comp. Rend.*, **98**, 1885.
[13] H. M. Dawson, *Trans. Chem. Soc.*, **89**, 1666 (1906); **95**, 370 (1909).
[14] Levallois, *Bull Soc. Chem.* (2) **43**, 83, 616 (1885).
[15] Levallois, *Comp. Rend.*, **98**, 372, 732 (1884); **99**, 431, 1027 (1884)
[16] Bechamp, *Ibid.* **99**, 1027, 1122 (1884); **100**, 279, 368 (1885).
[17] Willstatter & Zechmeister, *Ber.*, **46**, 2401 (1912).
[18] Schlossberger, *Journ. für prakt. Chem.*, **73**, 373 (1858)
[19] Lehner, *Zeit. für angew. Chem.*, **19**, 1584 (1906).
[20] Mulder, *Jahr. der Chem.*, 566 (1863).
[21] Haller, *Zeit. für Farben Ind.*, **6**, 126 (1907),

Mercerised Cotton.

It was first observed by Mercer[3–4] that cotton fibres shrink when they are treated with concentrated solutions of caustic soda. This shrinkage has been shown[7] to be caused by the action of internal stresses present in natural cotton fibres. If prevented from shrinking while under treatment with the alkali, the fibres acquire an increased lustre.[5–6] Lange[8] considered this lustre to be due to the smoothness of the surface of the mercerised fibres as compared with untreated cotton. Hübner & Pope[9] suggested that the formation of regular spiral grooves in the fibre during mercerisation was the cause of the lustre. This theory has been shown[7] to be untenable, Lange's theory being substantially correct. The shape of the cross-section of the mercerised fibres has been shown to have an important bearing on the lustre.[7]

The amount of caustic soda absorbed by cotton during mercerisation has been investigated by several workers.[11–15 38] Vieweg[13] observed change points in the curve of absorption but Miller [14] found the curve to be continuous. Clayton Beadle & Stevens[15] made some interesting observations on the absorption of caustic soda by regenerated cellulose which have an important bearing on this subject.

Mercerised cotton has properties which differ from those of ordinary cotton in the following manner:—

It grinds more pasty in the hollander,[16–17] dissolves quicker in solvents, gives a greater yield of benzoyl derivative,[18] gives nitrates more soluble in solvents[19] but giving less viscous solutions[20] and gives a blue colour with iodine with a less concentrated solution of sulphuric acid than ordinary cotton.[7] In the last case, the application of tension during mercerisation has been shown to modify the reaction.

All these properties are in agreement with the view that mercerisation produces distension of the fibre—colloid.

Mercerised cotton appears to revert towards its original condition on drying,[21 24 36] or on treatment with alcohol.[23] Green[22] considers this reversion to be due to anhydride formation, but the author thinks it is an ordinary case of gel-dehydration, since the same effect is produced by pressure without the application of heat or chemical re-agents.[25] A similar change is produced by pressure on wet unmercerised cotton,[26] the effect being much greater when heat also is applied.[26 27]

The internal structure of cotton fibres,[28–33] and the internal stresses present in them (A 12) are considerably modified by mercerisation: these changes persist when the fibres are dried.

The dying properties of cotton,[34 35] and its re-activity towards certain re-agents, are modified in a similar manner to that produced by caustic alkalies, when treated with solutions of sulphuric, hydrochloric[36] and nitric acids[37] and zinc chloride.[3 4]

(D) *Mercerised Cotton.*

[1] Cross & Bevan, *Researches*, I. p. 26.
[2] Gardener, *Mercerisation.*
[3] Mercer, *Life and Labours of John Mercer*, Parnell (Longmans, Green), 1884.
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[6] Thomas & Prevost, D. R. P., 85564 (1895).
[7] Harrison; *Journ. Soc. Dyers & Cols.*, **31**, 198 (1915).
[8] Lange, *Farber Zeitung*, 197 (1898).
[9] Hübner & Pope, *Journ. Soc. Chem. Ind.*, **22**, 70 (1903) ; **23**, 410 (1904)
[10] Hübner, *Ibid.*, **27**, 110 (1908).
[11] Gladstone, *Trans. Chem. Soc.*, **17**, (1862).
[12] Crum, *Ibid.*, **16**, 406.
[13] Vieweg, *Ber.*, **40**, 3876 (1907) ; **41**, 3269 (1908).
[14] Miller, *Ber.*, **40**, 4903 (1907) ; **41**, 4297 (1909) ; **43**, 3430 (1910).
[15] Clayton Beadle & Stevens, *Journ. Soc. Dyers & Cols.*, **30**, 244 (1914)
[16] Briggs, *Papier Fabrikant*, **5**, 2644 (1907).
[17] Cross, *Papier Zeitung*, **33**, 3246 (1908).
[18] Wichelhaus & Vieweg, *Ber.*, **40**, 441 (1907).
[19] Piest, *Zeit. fur angew Chem.*, **22**, 1221, 2012 (1908).
[20] Berl, *Zeit. fur Schiess and Sprengwesen.* **4**, 81 (1909).
[21] Copley, *Journ. Soc. Dyers & Cols.*, **24**, 72 (1908).
[22] Green, *ibid.*, **24**, 72 (1908).
[23] Hübner & Teltscher, *Journ. Soc. Ind.*, **28**, 641 (1909).
[24] Miller, *Ber.*, 728 (1911).
[25] Hübner, E. P., 12455 (1908).
[26] Harrison, E. P., 16276 (1908).
[27] Palmer, E. P., (1909), September.
[28] Crum, *Trans. Chem. Soc.*, **13**, 404 (1863).
[29] Frankel & Friedlander, *Mitl. d. k. Tech. Gew. Mus. Wien*, 326 (1898).
[30] Minajeff, *Zeit. Farben. Ind.*, 1 and 17 (1908).
[31] Minajeff, *Zeit. fur Farben and Textile Chem.*, **2**, 257 (1903) ; **4**, 81 (1905) ; **6**, 309, 345, **15**, 233, **16**, 252, **19**, 309 (1907) ; **7**, 1 (1908).
[32] Haller, *ibid.*, **8**, 125 (1907).
[33] Haller, *Koll. Zeit.*, **20**, 127 (1917).
[34] Justin Mueller, *Zeit. fur Farben and Textile Chem.*, **3**, 251, 332 (1904).
[35] Knecht, *Journ. Soc. Dyers & Cols.*, **24**, 68 (1908).
[36] Knecht, *ibid.*, **24**, 107 (1908).
[37] Knecht, *ibid.*, **12**, 89 (1891).
[38] Leighton, *Journ. phys. Chem.*, **20**, 32, 188 (1916).

Hydrocellulose.

Hot dilute mineral acids hydrolyse cellulose forming a pulverulent substance termed ' hydrocellulose ' [1–14] and a sugar having the same reducing power and optical activity as glucose.[16] [18]

Denham and Woodhouse[17] by the hydrolysis of methylated cellulose have obtained methyl glucoses. This points definitely to the conclusion that glucose is formed by the hydrolysis of cellulose, although Cross[19] considers this to be still an open question.

The author[15] has shown that hydrocellulose may exist in several different colloidal states and has suggested that it is a form of cellulose containing absorbed reducing bodies. Guignet's soluble cellulose[20] is probably a similar form of cellulose not containing reducing agents.

The action of chemical reagents on a solid structure would obviously be to attack the exposed surfaces and dissolve them away, gradually reducing the size of the solid particles, with consequent modification in colloidal state.

(E) *Hydrocellulose.*

[1] Cross & Bevan, *Cellulose.*
[2] Schwalbe, *Die Cellulose*, p. 211.
[3] Girard, *Ann. Chem. Phys.* (5) **24**, 542–370 (1881).
[4] Flechsig, *Zeit. Physiol. Chem.* **7**, 523 (1883).
[5] Vignon, *Comp. Rend.* **126**, 1355 (1888).

[6] C. Koechlin, *Bull. Soc. Mulhouse*, 55 (1888).
[7] Cross & Bevan, *Journ. Soc. Chem. Ind.* **12**, 966 (1893).
[8] Stern, *Trans. Chem. Soc.* **67**, 74 (1895).
[9] Tollens & Murmurow, *Ber.* **34**. 1431–4 (1901).
[10] Morck & Walker, *Journ. Franklin Inst.* 136 (1907).
[11] Schwalbe, *Zeit. fur angew Chem.* **20**, 2170 (1907).
[12] Buttner & Neumann, *ibid.* **21**, 26 9 (1908).
[13] Ost. & Wilkening, *Chem. Zeit.* **34**, 461 (1910).
[14] Cross & Bevan, *8th Int. Congress Applied Chem.* **13**, 101 (1912).
[15] Harrison, *Journ. Soc. Dyers & Cols.* **28**, 238 (1912).
[16] Willstatter & Zechmeister, *Ber.* **46**, 2401 (1913).
[17] Denham & Woodhouse, *Trans. Chem. Soc.* 1735 (1913); 2357 (1914); 244 (1917).
[18] Cunningham, *ibid.* 173 (1918).
[19] Cross & Bevan, *ibid.* 182 (1918).
[20] Guignet, *Comp. Rend.* **108**, 1258.
[21] Fort & Pickles, *Journ. Soc. Dyers & Cols.* **31**, 255 (1915).
[22] Briggs, *Journ. Soc. Ch. Ind.* 78 (1916).

Oxycellulose.

Oxidising agents attack cellulose, producing bodies[1–3 7 11–24] similar in many respects to hydrocellulose,[6 8 9 10 24 25 26] in fact no test has yet been found which definitely distinguishes between these substances. The suggestion has been made[26] that oxycellulose consists of a form of cellulose containing adsorbed reducing substances which may or may not be similar to those present in hydrocellulose.[15] It is interesting to note that oxycellulose is formed by the action of light on cellulose.[37 38]

Cross and Bevan[27 28] observed that bleached cotton retained the power of liberating iodine from potassium iodide much longer than the presence of a trace of hypochloride would account for.[30] They considered that a peroxide was formed. Ditz[29 32] made a similar observation in the action of ammonium persulphate on cotton. This effect may be due to adsorption by the fibre-colloid.[31 33]

A similar effect has been noticed in the action of ozone on cellulose.[34]

(F) *Oxycellulose.*

[1] Cross & Bevan, *Cellulose.*
[2] Schwalbe, *Die Cellulose*, pp. 221–257.
[3] Witz, *Bull. Rouen*, **10**, 447 (1882); **11**, 2210 (1883).
[4] Vetillart, *ibid.* **11**, 234 (1883).
[5] Permetier, *ibid.* **11**, 236 (1883).
[6] Schmid, *Dingler's Journ.* 250, 278 (1883).
[7] Cross & Bevan, *Trans. Chem. Soc.* **43**, 22 (1883); **46**, 206, 291, 897 (1884).
[8] Witz & Osmond, *Bull. Soc. Chem.* **45**, 309-15 (1886).
[9] Witz & Osmond, *Ber.* **19** (3), 318 (1886).
[10] Nastjukoff, *Bull. Mulhouse*, **62**, 493–510 (1892).
[11] Cross, Bevan & Beadle, *Ber.* **26**, 2520, (1893).
[12] Bull, *Trans. Chem. Soc.* **71**, 1090–1097 (1897).
[13] Vignon, *Bull. Soc. Chem.* (3) **19**, 790 (1898).
[14] Von Faber & Tollens, *Ber.* **32**, 2592 (1899).
[15] Bumcke & Wolffenstein, *Ber.* **32**, 2493 (1899).
[16] Nastjukoff, *Ber.* **33**, 2237 (1900).
[17] Nastjukoff, *Ber.* **34**, 719 (1901).
[18] Murmurow, Sack & Tollens, *Ber.* **34**, 1427 (1901).
[19] Vignon, *Bull. Soc. Chem.* (3) **25**, 136 (1901).
[20] Kurz, *Zeit. fur Farb. and Textilchemie*, **1**, 46 (1902).
[21] Vignon, *Bull. Soc. Chem.* (3) **29**, 513 (1903).
[22] Berl & Klaye, *Zeit. Schiess and Sprengwesen*, **2**, 381, 387 (1907).
[23] Ditz, *Journ. Prakt. Chem.* **78**, 348 (1908).

[24] Scholl, *Ber.* 1312 (1911).
[25] Ermen, *Journ. Soc. Dyers and Cols*, **26**, 266 (1910); **27** (1911).
[26] Harrison, *Journ. Soc. Dyers and Cols.* **28**, 359 (1912), 132.

Cellulose Peroxide.

[27] Cross & Bevan, *Zeit. angew. Chem.* **19**, 2101 (1906).
[28] Cross, Bevan & Briggs, *ibid.*, **20**, 570 (1907).
[29] Ditz, *Chem. Zeit.*, **31**, 833, 844, 857 (1907).
[30] Heinke, *ibid.*, **31**, 974 (1907).
[31] Zimmermann, *Zeit. fur angew. Chem.* **20**, 1286 (1907).
[32] Ditz, *Journ. prakt. Chem.* **78** 343 (1908).
[33] Grandmougin, *Chem. Zeit.*, **32**, 242 (1908).

Cellulose Ozonide.

[34] Dorée, *Trans. Chem. Soc.* **101**, 497 (1912).

Action of Light on Cellulose.

[35] Hartley, *Proc. Roy. Soc.* B **78**, 385; **80**, 376.
[36] Hartley, *Trans, Chem. Soc.* **63**, 243 (1893).
[37] Harrison, *Journ. Dyers and Cols.* **28**, 225 (1912).
[38] Dorée & Dyer, *ibid.*, **33**, 19 (1917).

Cellulose Nitrates.

When cellulose is treated with a mixture of sulphuric and nitric acids, esters are formed containing nitrogen in quantities varying with the conditions of treatment.[1–5 7 9 11 12 14 23] Many authors[6 8 9] have attempted to classify the products, according to degree of nitration, into nitrates of definite molecular composition but there seems to be no break in the curve representing the amount of nitrogen introduced by different concentrations of acid.[11 15 17] The suggestion has been made[16] that nitrocelluloses are adsorption compounds but this view does not appear to have been substantiated.[17] There is little doubt that true esters are formed, but as the cellulose is solid during treatment, the reaction must take place from the exposed surfaces, whether external or within the porous structure of the fibre, and the degree of nitration must be dependent on the colloidal state of the fibre substance.

The viscosity of solutions of nitrocellulose[11 13 18 19 20 21] vary with the conditions of preparation. A nitrocellulose after solution and reprecipitation has been shown to give a less viscous solution than one directly dissolved.[18] Similar changes have been observed with rubber solutions.

The behaviour of nitrated cotton towards polarised light has been investigated by several authors[13 18 21 22] and many interesting points brought forward.

(G) *Cellulose Nitrates.*

[1] Cross & Bevan, *Cellulose*, p. 38.
[2] Schwalbe, *Die Cellulose*, p. 270.
[3] Schonbein, *Comp. Rend.* **23**, 678 (1846).
[4] Otto, *ibid.*, **23**, 807 (1846).
[5] Crum, *Proc. Phil. Soc. Glasgow*, 183 (1847).
[6] Eder, *Ber.*, **13**, 169 (1880).
[7] Knecht, *Journ. Soc. Dyers & Cols.*, **12**, 89 (1891).
[8] Veielle, *Comp. Rend.*, **95**, 132 (1883).
[9] Liebschutz, *Mon. Sci.*, p. 119 (1891).
[10] Vignon, *Comp. Rend.*, **126** (1898).

[11] Lunge, *Journ. Amer. Chem. Soc.*, **23**, 527 (1901).
[12] Berl & Klaye, *Mon. Sci.* (4), 23, 103.
[13] Mosenthal, *Journ. Soc. Chem. Ind.*, 292 (1904).
[14] Cross & Bevan, *Cellulose* (pp. 38–41) *Researches*, 1895–1900 ; p. 43 ; 1900, 3, p. 97.
[15] Saposchnikow, *Journ. Russ. Phys. Chem. Soc.*, **35**, 669 (1904) ; **36**, 518 (1905) ; **38**, 1186 (1906).
(See also *7th Internal Cong. Appl. Chem.*, London, p. 19).
[16] E. Justin Mueller, *Koll. Zeit.*, **2**, 49 (1907).
[17] Arthur Muller, *ibid.*, **2**, 173 (1907).
[18] Mosenthal, *Journ. Soc. Chem., Ind.* 443 (1907).
[19] Piest, *Zeit. Angew. Chem.*, **22**, 1215 (1908) ; **23**, 1009 (1910).
[20] Berl, *Zeit. f. Scheiss and Sprengwesen*, **4**, 81 (1909) ; **5**, 254 (1910).
[21] Schwartz, *Koll. Zeit.*, **12**, 32 (1913).
[22] Ambronn, *Koll. Zeit.*, **13**, 200 (1913).
[23] Knecht & Lipschitz, *Journ. Soc. Chem. Ind.* **33**, 116 (1914).

Organic Esters of Cellulose. Cellulose Acetates.

Cellulose forms esters of acetic acid when treated with acetic anhydride in presence of condensing agents.[1–12] The maximum amount of acetyl groups which can be introduced without modification of the cellulose complex corresponds to one half of the number of carbon atoms present in the cellulose. It is possible to introduce more acetyl groups but considerable modification in the cellulose is produced.

The solubility of celulose acetates and the viscosity[10] of its solutions varies with the conditions of preparation in a more irregular manner than the nitrates. Even under apparently identical conditions, different results are sometimes obtained. The ease with which the colloidal state of the cellulose in cotton fibres is changed is possibly the explanation of those differences.

Cellulose Formate.

Cellulose forms derivatives with formic acid quite readily in the presence of condensing agents.[14–19] It has been stated[20] that cellulose formate is produced when oxalic acid solution is dried on cotton.

The properties of cellulose formates have not yet been thoroughly studied.

Of other esters of cellulose the following have been prepared :—

Cellulose propionate,[21] butyrate,[22] aceto-butyrate,[22] palmitate,[22] phenyl-acetate,[22] phospho-formate,[23] aceto-nitrate,[24] aceto-sulphate,[25] nitro-sulphate,[26 27 28] sulphonates, etc.

Recently, methylated celluloses[30 31] have been prepared, and their products of hydrolysis carefully studied. Nastjukoff[32] claims to have prepared phenylated celluloses.

(H) *Cellulose Acetates.*

[1] Cross & Bevan, *Cellulose*, p. 34.
[2] Schwalbe, *Die Cellulose*, p. 316.
[3] Worden, *Nitrocellulose Industry*, pp. 984–1004.
[4] Schutzenberger, *Comp. Rend.* **61**, 488 (1869) ; **68**, 814 (1870).
[5] Franchimont, *Ber.* **12**, 1264, 1941, 2099 (1879).
[6] Cross & Bevan, *Trans. Chem. Soc.* **57**, 1 (1890) ; **67**, 433 (1895).
[7] Thiele, *Journ. Soc. Dyers & Cols.* **24**, 294 (1908).
[8] Cross & Briggs, *ibid.* **24**, 189 (1908).
[9] Schwalbe, *Zeit. angew. Chem.* **23**, 435 (1910).

[10] Knoevenegal, *ibid.* **24**, 504 (1911).
[11] Patents. Compare Suvern, *Die kunstliche Seide*, Berlin (1900).
[12] Compare Marsden, *Journ. Soc. Dyers & Cols.* **21**, 103 (1905).
[13] Compare Worden, *Journ. Soc. Chem. Ind.* **31**, 1064 (1912).

Cellulose Formate.

[14] Berl & Smith, *Ber.* **40**, 903 (1907).
[15] Woodbridge, *Journ. Amer. Chem. Soc.* **31**, 1070 (1909).
[16] Deming, *ibid.* **33**, 1519 (1911).
[17] Worden, *Journ. Soc. Chem. Ind.* **31**, 1064 (1912).
[18] Worden, *Nitrocellulose Industry*, pp. 1004–1006.
[19] Cross, *Trans. Chem. Soc.* **99**, 1450 (1911).
[20] Knecht, *7th Int. Cong. App. Chem., London*, 1909.
[21] Cellulose Propionate. See refs. 14 & 15.
[22] Cellulose Butyrate. *Aceto-Butyrate, palmitate and phenyl-acetate. Henckel*, D.R.P. 12817/00.
[23] Cellulose Phospho-formate. *Vereinigte Glanzstoff Fabr.* E.P. 29246/10; 309/11.
[24] Cellulose Aceto-Nitrate. Berl. & Watson Smith, *Ber.* **40**, 903 (1907).
[25] Cellulose Acetosulphate and Acetobenzoate. Cross, Bevan & Briggs, *Ber.* **38**, 1859, 3561 (1905).
[26] Cellulose Nitrosulphate. Cross & Bevan, *Researches*, 1900–5, pp. 51–53.
[27] Cellulose Nitrosulphate. Cross, Bevan, & Jenks, *Ber.* **34**, 3496 (1908).
[28] Cellulose Nitrosulphate. Hake and Lewis, *Journ. Soc. Chem. Ind.* **24**, 374, 914 (1905).
[29] Benzoate. Cross & Bevan, *Cellulose*, p. 32; *Researches*, I. p. 34.
[30] Methylated Celluloses. Denham & Woodhouse, *Trans. Chem. Soc.*, 1735 (1913); 2357 (1914); 244 (1917).
[31] Ethylated Celluloses. Lilienfeld, F.P. 447974 (1912).
[32] Phenylated Celluloses. Nastjukoff, *Journ. Russ. Phys. Chem. Soc.* **34**, 231, 505 (1902). Compare *Journ. Soc. Chem. Ind.* Abstracts 1302 (1902); 414 (1903); 282 (1907).

Viscose.

When treated with caustic soda and carbon disulphide cellulose forms a xanthogenate soluble in water.[1–7] A solution of this substance increases in viscosity on standing and eventually sets to a jelly. This change is known as ripening, and is considered by Cross and Bevan to be due to the formation of compounds of increasing complexity. This phenomenon appears to be quite analogous to the setting of a gelatine jelly, although recent patents[8] indicate that the oxygen of the air may play some part in it. It is interesting to note that if the cellulose is left in contact with the caustic soda for some time before conversion into viscose a less viscous solution is produced.[9]

(I) *Viscose.*

[1] Cross & Bevan, *Cellulose*, p. 25; *Researches*, pp. 27, 107.
[2] Schwalbe, *Die Cellulose*, p. 332.
[3] Cross, Bevan, & Beadle, E.P. 8700 (1892).
[4] Cross, Bevan, & Beadle, *Trans. Chem. Soc.* **63**, 837 (1893).
[5] Cross, Bevan, & Beadle, *Journ. Soc. Chem. Ind.* **12**, 498 (1893).
[6] Cross, Bevan, & Beadle, *Ber.* **34**, 1513 (1901).
[7] Beltzer, *Koll. Zeit.* **8**, 177 (1911); **9**, 76, 120 (1911).
[8] Courtaulds, Glover, & Wilson. E.P. 13, 005 (1914); 14675 (1914).
[9] Cross & Bevan, *Researches* (1900–5), p. 107.

Artificial Silk.

The preparation of artificial silk[1] is dependent on the coagulation of a cellulose solution, and it is found that the viscosity of the solution influences the nature[2] [3] of the fibres obtained.

An interesting investigation has recently been carried out by Clayton, Beadle & Stevens on the swelling of artificial silk in caustic soda solutions.[4 5] It was found that the swelling increased with the concentration of alkali up to a certain point and then decreased. This change is very similar to that observed by Procter with gelatine and hydrochloric acid. Procter's method of investigation cannot be applied in this case since the concentration of alkali used is too high. It was shown that the addition of sodium chloride to the caustic soda diminished the swelling and adsorption of alkali. The author found that if the artificial silk was first treated with the caustic soda and then with a salt solution the amount of swelling was considerably decreased, but practically no caustic soda passed into the salt solution. It is, of course, known that sodium chloride 'salts out' caustic soda from solution.

(J) *Artificial Silk.*

[1] Suvern, *Die Kunstliche Seide*, Berlin (1900).
[2] Herzog, *Untersuchung der naturlichen und Kunstlichen, Seiden* (1910).
[3] Gaidukow, *Koll. Zeit.*, **6**, 260 (1910).
[4] Clayton, Beadle & Stevens, *8th Int. cong. Chem.* 13, p. 25.
[5] Clayton, Beadle & Stevens, *Journ. Soc. Dyers & Cols.*, **30**, 244 (1914).
[6] Ost, *Zeit. f. angew. Chem.*, 31, p. 141 (1918).
[7] Wilson, *Journ. Soc. Chem. Ind.*, 817 (1917).

Wool.

The products formed by the hydrolysis of wool have been determined,[1] but nothing is known of the constitution of the substances of the wool fibre itself. The presence of a free amido group in the substance of the wool fibre has been discussed from time to time without any very definite conclusions being arrived at.[2 3 4 13] It has recently been shown that wool fibres are not chemically homogeneous, the outer layers being more resistant to the action of chemical reagents than the inner parts.[5 6]

By treatment of wool with solutions of caustic alkalies a colloidal solution is obtained,[7] which forms precipitates with dyestuffs.[8–14] These precipitates have been considered to be definite chemical compounds. The process of precipitation reminds one more of the coagulation of colloidal solutions than of chemical combination.

The colloidal state of wool fibres is considerably changed by boiling in water, the fibres becoming more plastic; changes in the internal strains are also produced.[9 10]

When subjected to beating in presence of solutions of soap or of acids, wool fibres become matted together, the process being known as felting, fulling or milling. For many years felting has been considered to be due to the interlocking of the serrations present in wool fibres. This theory was supported by the fact that in some cases fibres with less serrations felted less easily than others with more, and that treatment with chlorine[11] removed the serrations and prevented felting. There are, however, wool fibres having practically no serrations which can be felted, although with difficulty, but which are also prevented from felting by treatmnt with chlorine. Another theory has been brought forward[17] that the wool fibres become plastic and adhere together when subjected to beating. The fact that a fabric made of tightly spun, straight wool fibres is very much more difficult to felt than one made of more loosely-spun material appears

against this theory, since the closer contact obtained in the first case should assist this adhesion of fibres.

The author is of the opinion that felting is due mainly to the interlocking of fibres caused by the beating of the wool while in an elastic condition. Chlorine reduces this elasticity and makes the wool more plastic.

Mechanical pressure produces considerable changes in wool, particularly when containing moisture and at a high temperature.[9]

The adsorption of acids by wool has been determined by numerous workers.[12–16] The work of Procter (*see* First Report) on the action of acids on gelatine led other chemists[13] to consider that wool formed definite compounds with acids. Exactly as in the case of the adsorption of caustic soda by cotton and the nitration of cotton, peaks were noticed in the curve of adsorption.[13] In the two examples of cotton more recent work has shown that the curves are continuous, and it is certain that the same will apply to wool. The author attempted to apply Procter's methods to wool, but no results of any value were obtained. The amount of swelling in the case of wool is very small compared with that shown by gelatine. The osmotic effect which was expected from Procter's theory did not produce any changes in volume of the wool fibre; it may, however, have produced a change in the internal stresses present in the fibre, but this could not be determined.

(K) *Wool:*

[1] Abderhalden, *Journ. Physiol. Chem.* **46**, p. 31.
[2] Prudhomme, *Rev. Gen. Mat. Col.* 209 (1898).
[3] Kann, *Färber Zeit.* **25**, 73 (1914).
[4] Gabhard, *Färber Zeit.* **25**, 279–283 (1914).
[5] Naumann, *Zeit. fur angew. Chem.* **30**, 135, 297, 305 (1917).
[6] Allworden, *Zeit. angew. Chem.* **29**, 77, 78 (1916).
[7] Champion, *Comp. Rend.* **72**, 330.
[8] Knecht & Appleyard, *Journ. Soc. Dyers & Cols.* **15**, 71 (1889). (Dye compounds.)
[9] Harrison, *Proc. Roy. Soc.* **A. 94**, 460 (1918).
[10] Herzoz, *Chem. Zeit.* **40**, 528 (1916).
[11] Pearson, *Journ. Soc. Dyers & Cols.* **25**, 81 (1909).
[12] Georgievics, *Zeit. Physiol. Chem.* **87**, 669 (1914).
[13] Fort & Lloyd, *Journ. Soc. Dyers & Cols.* **30**, 5, 73 (1914).
[14] Fort & Lloyd, *Ibid.* **30**, 297 (1914). (Indigo compound.)
[15] Harrison, *Ibid.* **34**, 57 (1918).
[16] Gee & Harrison, *Trans. Faraday Soc.* (*April*, 1910).
[17] Justin Mueller, *Koll. Zeit.* 114 (1909).
[18] Miller & Tallmann (Strength & Elasticity of Wool), *J. agric. Res.* **4**, 379 (1915).
[19] Hardy, *Ibid.* **14**, 285 (1918).
[20] Hartshorne, *Trans. Nat. Assoc. Cotton Manuf.* **79**, 194–225 (1905); **90**, 281–319 (1911).
[21] Woodmansey, *Journ. Soc. Dyers & Cols.*, **34**, 227 (1918).

Silk.

A large amount of work has been carried out on the products of hydrolysis of different kinds of silk.[1–2] The silk fibre in its natural condition consists of two substances, sericine and fibroine, very similar in chemical nature. The sericine is dissolved from the fibroine by the action of dilute alkalies. Attempts have been made from time to time to fix this sericine by means of formaldehyde[3–4] in order to avoid the loss in weight of the silk, but little is known regarding the value of this process.

Silk is modified by boiling in water in a similar manner to wool.[5] The effect of mechanical pressure is also similar with these two fibres.

Colloid chemical investigations have been made[6] with the substance present in the glands of the silkworm from which the silk is spun. The colloid present in these glands coagulates on standing, more quickly on heating or freezing or by treatment with dilute acids, a tough gelatinous mass being formed. It is interesting to note that the coagulation is accelerated by mechanical strain, and the suggestion has been made[6] that the solidification of the silk as spun by the silkworm is due to the mechanical strain exerted during ejection of the viscous secretion of the silk gland through the spinning orifices. This may have some connection with the double refraction shown by silk fibres.[5]

(L) *Silk:*

[1] Fischer, *Zeit. Physiol. Ch.* p. 126 (1907).
[2] Abderhalden, *Zeit. Physiol. Chem.* **66**, 13—18 & 910 and numerous other articles.
[3] Clavel & Lindermeyer, F.P. 451, 897 (1912).
[4] Cardazzi, F.P. 457, 326 (1913).
[5] Harrison, *Proc. Roy. Soc.*, A., **94**, 460 (1918).
[6] Foa, *Koll. Zeit.* **10**, 7—12 (1912).
[7] Farrell, *Journ. Soc. Dyers & Cols.* 70 (1905). (Action of hydrochloric acid.)
[8] Sansone, *Rev. Gen. Mat. Col.* 194 (1911). (Action of formic acid.)
[9] Hohnel, *Journ. Soc. Chem. Ind.* **2**, 172. (Diameter of silk fibres.)
[10] Wardle, *Tussur Silk.*
[11] Vignon, *Recherches sur la soie, Lyon* (1892).
[12] Rossinski, *Bull. du Labor de la soie, Lyon* (1895).
[13] Franceson, *Etudes sur la filature de la soie, Lyon* (1890).
[14] Collomt, *Journ. de Physik.* (1785).
[15] Bolley & Schoch, *Dingl polyt Journ.* 196 (1870).
[16] Cramer, *Journ. fur prakt. Chem.* **96**.
[17] Persoz, *Mon. Sci.* **1**, 597.
[18] Mills & Takamine, *Trans. Chem. Soc.*, p. 142 (1881). (Absorption of acids.)
[19] Silberman, *Die Seide.*

Sizing.

Very little work of any importance has been done with respect to the sizing of textile materials, but a considerable amount of work has been done on the materials used in this process. The work carried out on glue and gelatine has been fully dealt with by Procter in the first report. Practically all the work done on starch has been considered by Brown[1] and by Stocks.[2] The characteristic blue colour produced when iodine is added to starch has been shown to be due to colloidal iodine,[3] and many other substances have been found to give the same reaction.[14]

The changes undergone by starch during boiling are of great importance in relation to sizing and finishing and have received considerable attention.[4–12] The addition of salts has been shown to influence these changes.[5–6]

The so-called sizing properties of starch are somewhat obscure. The process of sizing is carried out for the specific purpose of assisting in the weaving of fabrics, and the advantages of any particular sizing material can, at present, only be determined by a practical test.[13] The relationship between the mechanical properties of the sized yarns and the physical properties of the sizing materials has never been determined. This is mainly due to the difficulty of

measuring those mechanical properties of sized yarns which determine their value in weaving.

(M) *Sizing, Starch, &c.*

[1] *See* Brown, First Report, p. 38.
[2] Stocks, First Report, p. 46.
[3] Harrison, *Koll. Zeit.* **9**, 5 (1911).
[4] Harrison, *Journ. Soc. Dyers & Cols.* **27**, p. 84 (1911).
[5] Samec, *Kolloidchem. Beiheft.* **3**, 123 (1911).
[6] Samec, *ibid.* **4**, 132 (1912).
[7] Samec & Hoefft, *ibid.* **5**, 141 (1913).
[8] Samec, *ibid.* **6**, 23 (1914).
[9] Samec & Jencic, *ibid.* **7**, 127 (1915).
[10] Samec, *ibid.* **8**, 33 (1916).
[11] Rakowski, *Koll. Zeit.* **9**, 225 (1912); **10**, 22 (1912); **11**, 19, 51, 269 (1913).
[12] Harrison, *Journ. Soc. Dyers & Cols.* **32**, 40 (1916).
[13] Whowell *Text. Inst. Journal* **2**, 43 (1911).
[14] Barger & Starling, *Trans. Chem. Soc.*, 441 (1915).
[15] Barger & Field, *Trans. Chem. Soc.*, 1394 (1916).

Scouring (Soap, &c.).

The scouring of textiles is mainly a colloid-chemical process. In the case of cotton the impurities to be removed are fats and colloidal matters usually termed pectic substances. These latter form colloidal substances in alkali, by which they are removed from the cotton. In recent patents[24] substances of colloidal character, starch and albumenoids, are used in conjunction with caustic alkalies as scouring agents, and apparently these substances act as protective colloids during the scouring process.

In the case of wool the impurities consist mainly of fat, although some protein matters are present in the "suint." The removal of this fat is effected by a dilute solution of soap.

The nature of the process of scouring has recently been investigated from the colloid-chemical standpoint[20] and numerous important points deduced.

The impurities in silk consist mainly of albumenoid and are removed by dilute solution of soap.

(N) *Scouring Soap, &c.*

[1] Chevreul, *Recherches sur les Corps gras d'origine animale Paris* (1823).
[2] Krafft, *Ber.*, **27**, 1747 (1894); **28**, 2566 (1895); **29**, 1328 (1896); **32**, 1584, 1899.
[3] Kahlenberg & Schreiner, *Zeit. f. Phys. Chem.*, **27**, 559 (1899).
[4] Cornish, *ibid.*, **31**, 42 (1899).
[5] Donnan, *ibid.*, **31**, 44 (1899).
[6] Donnan & White, *Trans. Chem. Soc.*, 1668 (1899).
[7] Browden, *ibid.*, 191 (1899).
[8] Goldschmidt, *Seifen fabr.*, 1247 (1902).
[9] Smits, *Zeit. f. Phys. Chem.* **45**, 608 (1903).
[10] Leimdorfer, *Seifensieder Zeitung Ausgberg* (1906).
[11] Meyer, Schaeffer & Terroine, *Comp. Rend.*, **146**, 484 (1907).
[12] Spring. *Koll. Zeit.*, **4**, 162 (1909); **6**, 11, 109, 164 (1910).
[13] Leimdorfer. *Kolloidchem. Beihefte*, **2**, 243 (1910).
[14] Donnan & Potts, *Koll. Zeit.*, **7**, 208 (1911).
[15] Reychler, *ibid.*, **12**, 18, 277 (1913); **13**, 252 (1914).
[16] Arndt & Schiff, *Kolloid. Beihefte*, **6**, 201 (1914).
[17] Kurzmann, *ibid.*, **5**, 433 (1914).
[18] McBain, *Trans. Faraday Soc.*, **9**, 99 (1913).

[19] Fischer & Hooker. *Koll. Zeit.* 18, 129 (1916). (Casein Solutions.)
[20] Shorter, *Journ. Soc. Dyers & Cols.*, **31**, 64 (1915); **32**, 90 (1916); **34**, 136 (1918).
[21] Shorter & Ellingworth, *Proc. Roy. Soc.*, A, **92**, 232 (1916).
[22] Pickering, *Trans. Chem. Soc.*, **111**, 96 (1917).
[23] Shorter & Harrison, *Journ. Soc. Dyers & Cols.*, **34**, 163 (1918).
[24] McPherson & Heys, *E.P.*, 5620 (1909); 20089 (1909); 8178 (1915).
[25] McBain & Taylor, *Ber.* **43**, 321 (1910).
[26] McBain & Taylor, *Zeit. phys. Chem.*, **76**, 179 (1911).
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Dyeing.

The large amount of work carried out on dyeing has already been fully considered by King in the first report. The electrical theory of dyeing has recently been discussed at some length.[3] In its present condition[2] four factors are taken into account.

1. Molecular movement, by which dye molecules or particles transport themselves on to the fibre or into its pores. In true solution, this process is usually known as diffusion and must be taken into account in all theories of dyeing. In colloidal solutions the same thing occurs but to a less extent.

2. The electrical charge on the fibre and on the dye. The potential of this charge has been measured under several conditions as regards nature and concentration of added electrolytes. The nature of this contact potential has received much discussion; some chemists consider it to be due to residual valency. The opposite view that valency is the direct result of the electrical construction of elements is more likely to be true. In any case Bragg's models of crystals show that the surfaces of solids must behave differently from the bulk of the material.

3. The size of the pores in the fibre.

The presence of these pores has been directly proved by ultramicroscopic examination and indirectly by the fact that colloidal solutions can penetrate to a considerable extent into the fibres. The idea that dyes are imbibed into the cavities and pores of fibres by capillary attraction was put forward by Crum more than 50 years ago. The manner in which the dyes were fixed in those pores was, however, not explained by Crum, but has been explained as a case of electrical coagulation.

The increased dyeing produced with cotton on mercerisation has been shown to be due to changes in the colloidal state of the fibre as well as electrical charge. The effect of drying on mercerised cotton is to reduce its dyeing capacity; this has been explained as being due to reversion of the changes produced by mercerisation.

4. The size of the dye particles.

It is obvious that the extent to which dye particles can penetrate into porous substances must depend on their size. The rapidity of coagulation is also dependent on the size of the particles.

By the inclusion of these four factors, the electrical theory appears to explain most cases of dyeing; its value is recognised mostly in the case of direct colours where chemical theories have failed.

Printing.

The printing of textile fabrics is carried out by applying a viscous solution by means of an engraved roller to the fabric. Many interesting colloid-chemical phenomena are met with in the preparation of the viscous printing pastes. Even to-day there is a considerable amount of secrecy exercised in the preparation of these pastes, partly as regards the materials employed, but more particularly in the manner of mixing them. There is little difficulty in ascertaining the ingredients by chemical analysis, and by the help of colloid chemistry the order in which the ingredients must be mixed can readily be decided. Materials which precipitate one another should first be mixed with the protective colloid, starch, tragaganth, &c.

The subsequent fixation of the printing colour by steaming, particularly in the case of non-mordant dyes, has been shown to be due to the swelling of the fibre by the action of the steam.[1 2, and 4] The fixation of colours from pastes containing both colour and mordant is undoubtedly due to coagulation, as the result of reduction in the protective power of the colloids at high temperature. [Compare 3]

Finishing.

The finishing of textile fabrics is an art to which very little science has been applied. The effects of the mechanical treatments to which fabrics are subjected during finishing[1] have only recently been investigated.[2] The main factors are mechanical pressure, heat and moisture. The effect of moisture is to increase the degree of swelling of the fibre, and this is greater the higher the temperature. Pressure decreases the swelling in the direction at which it is applied. Permanent finishes are produced by processes which reduce the swelling capacity of the fibre colloids.

(O) *Dyeing.*

[1] Compare King, *First Report*, p. 20.
[2] Harrison, *Journ. Soc. Dyers and Cols.*, **27**, 279 (1911).
[3] Harrison, *ibid.* **34**, 97, 127 (1918).
[4] Craven, *ibid.* **34**, 128 (1918).
[5] Fort, *ibid.* **34**, 124 (1918).
[6] Haller, *Koll. Zeit.*, **23**, 100 (1918).

(P) *Printing.*

Compare *First Report* Article by Stooks. 46–78
[1] Justin Mueller, *Koll. Zeit.*, **5**, 233 (1909).
[2] Justin Mueller, **7**, 40 (1910).
[3] Harrison, *Koll. Zeit.*, **9**, 5 (1911).
[4] Haller, *Kolloidchem, Beihefte*, **8**, 1 (1916).
[5] Haller, *Koll. Zeit.*, **23**, 100 (1918).

(Q) *Finishing.*

[1] See Article in *Journ. Soc. Dyers and Colourists*, **29**, 117 (1913).
[2] Harrison, *Textile Inst. Journal* (1916).

REPORT ON THE PART PLAYED BY COLLOIDS IN AGRICULTURAL PHENOMENA.

By E. J. Russell, D.Sc., F.R.S., *Director of the Rothamsted Experimental Station.*

Agricultural chemists only slowly recognised the part played by colloids in the soil. For many years the soil was regarded as a mass of crystalloid mineral matter, and in discussions of its properties it was treated as if it were sand mingled with certain soluble salts and organic matter. Sand cultures were commonly adopted in pot work; sand particles were used in experiments on the physical properties of the soil; and in the early attempts at mathematical analysis the particles were supposed to be spherical and impenetrable, though this assumption was recognised as an approximation only. As experimental results and deductions accumulated, it became obvious that there was a wide discrepancy between the properties expected and those actually found in natural soils. It therefore became necessary to re-examine the fundamental propositions.

The first demonstrations of the unsoundness of the old views came from the Dutch investigator van Bemellen. It had long been known that soil possessed the remarkable property of absorbing certain soluble substances from their solutions: ammonia was taken from ammonium sulphate solution, potash from potassium sulphate, and so on. It was this property that justified the use of soluble salts as artificial fertilisers. The first explanation was offered by Way, who supposed that the process was a simple chemical reaction of the double decomposition type, and he assumed the existence in the soil of a series of reactive silicates in order to account for the observed phenomena. Subsequent writers, adopting the simple expedient of keeping away from the soil, elaborated the properties of these double silicates; and when. at a later date, mineralogists directed attention to the zeolites, some of the agricultural chemists assumed that these substances existed in quantity in the soil and were the reactive constituents in question.

Shortly after Way had offered his chemical hypothesis Liebig advanced a physical explanation. He supposed that soil had some power of attracting dissolved salts similar to the power possessed by charcoal for condensing gases. Only the substances physically held in the soil were considered of immediate value to the plant, although the chemically combined substances might be a reservoir in maintaining supplies.

Further investigations showed that neither explanation was quite sufficient: Knop therefore combined the two hypotheses and explained the absorption of acids as a chemical combination with iron or aluminium oxides, and the removal of bases partly as a physical attraction and partly as a chemical combination with silica or double aluminium silicates. But the compromise was not very satisfying and aroused little enthusiasm; moreover, it did not help to account for the ever increasing number of ap-

parently abnormal phenomena. Later on van Bemmelen proved that the phenomena were precisely similar to those shown by colloids, and argued that the soil must be treated as a colloid. This view was generally accepted by those who read his papers. Unfortunately, van Bemellen's work was published in German, and the translation from his own language was not altogether happy—rather giving the impression of a long drawn tedious memoir on an unimportant subject. A good English translation is very desirable: the papers belong to the classics of agricultural chemistry. Van Bemellen did not at once arrive at the colloid explanation; he first accepted Way's chemical explanation, and, indeed, devised a method for estimating the double silicates present. Later on, however, he made extensive studies of absorption by simple gels, silica, alumina, ferric hydroxide, tin hydroxide, etc., and found it closely to resemble absorption by soils: other studies of colloids were made, and in each case the similarity to soil phenomena was so close as to leave no doubt that soil was essentially a colloid and soil adsorption simply a manifestation of its colloidal properties.

This new idea was soon found to explain many of the old discrepancies. Chemists had several times attempted to bring the phenomena of absorption equilibrium into line with those of chemical equilibrium, but the equations would not fit except for a narrow range of concentrations.

When, however, the absorption formula is used, a much closer fit can be obtained: Weigner has gone over the recorded data and shown that they all agree with the ordinary equation,

$$\frac{y}{m} = Kc^{\frac{1}{p}}$$

the constants having the following values:—

Absorbent.	Solute.	K	$\frac{1}{p}$	Worker.
Garden soil	NH_4Cl	0·0948	0·039	Henneberg and Stohmann.
„ „	NH_4Cl	0·131	0·424	
Nile sediment	NH_4Cl	0·489	0·399	Armsby.
Permutite ... (artificial)	NH_4Cl	2·823	0·398	Wiegner.
Sodium zeolite (artificial)	$CaCl_2$	2·487	0·317	Armsby.
Zeolite ... (artificial)	LiCl	24·419	0·414	Campbell.
Soil	NH_4OH	0·0994	0·434	Brustlein.
„	NH_4OH	0·147	0·461	
„	NH_4OH	0·054	0·386	

It is still, however, necessary to account for the fact that the absorbed bases displace an equivalent amount of some other bases from the soil—a procedure which would be unnecessary if nothing but adsorption were involved. This is done by supposing that only the hydroxide is absorbed: the acid radicle in general is not: it therefore dissolves out some of the bases from the soil. As this is a purely chemical reaction the amount of base brought out is equivalent to the acid set free, *i.e.*, to the amount of base adsorbed.

This view is found to account for all the phenomena as yet recorded. Moreover, it explains the difficulties that have attended the study of the soil solution or the liquid phase in the soil. Chemists now realise that the colloids profoundly affect the composition of the liquid phase, and they are devoting considerable time and ingenuity to the problem of extracting typical samples for investigation. Centrifugal methods have been tried, but they are troublesome in application. Displacement methods would be easier if one could be sure that the adsorption relationships were not being disturbed. Morgan claims that paraffin oil is both effective and simple in use. A pressure method is in use in Ramann's and also in van Zyl's laboratories, especially for soils containing much clay or humus: 3 kgms. of soil are subjected to a pressure of 300 kilos per sq. cm. In view of the great importance of the soil solution in the nutrition of plants, it is a matter of vital necessity to discover the laws governing its composition, the influence of manuring, climate and soil treatment.

Thus it is known that sodium salts liberate potassium from the soil: lime has also the same effect. Regarded as adsorption effects the phenomena are much easier to explain than are simple chemical reactions. The technical importance of a full understanding of the phenomena is considerable. There is, however, a school of chemists who regard the whole phenomena as chemical, and adhere to the hypothesis of reactive zeolites: Gedrortz in Russia, and von Rothmund and Kornfeld in Germany.

The Action of Acids on the Soil.

Agricultural chemists have long hoped that soil analysis might guide the farmer in drawing up a system of manuring. Unfortunately, this hope has proved largely illusory: the problem is complicated by the fact that at least five or six factors enter into soil fertility, of which the chemical composition of the soil is only one. But there is another source of trouble well recognised by agricultural chemists: the selection of a method for the extraction of the plant nutrients in the analytical process.

The first methods founded wholly on mineral analysis, involved the use of strong acids and proved of little value in this country. A marked improvemnet was effected when dilute acids were substituted for strong acids, but many anomalous cases still arose: in particular, no two acids ever gave the same result, nor even did different concentrations of the same acid. The underlying assumption always was that the soil was a mass of mineral fragments with the phosphates, etc., in the ordinary mineral form. All attempts to interpret the action of dilute acids on soil phosphates as an ordinary chemical reaction failed.

Russell and Prescott have studied the reaction between dilute acids and the phosphates in the soil and find that it can be interpreted satisfactorily as a simple solvent followed by an adsorption. The solvent action is practically the same for nitric, hydrochloric, and citric acids of equivalent strengths, and appears to be the normal action of an acid on a phosphate. The reverse reaction

is the typical adsorption shown by colloids, and can be expressed by the equation which has been found to fit so many of them. It is considerably influenced by the acid, being greater in the presence of the mineral acids than of the organic acids. The amount of phosphorus compound actually brought out is the difference between the direct and the reverse action. Thus, hydrochloric acid dissolves out a certain amount of phosphate, but considerable adsorption takes place, so that the net amount left in solution is only small. Citric acid dissolves out the same amount of phosphate, but there is much less adsorption, and therefore the amount left in solution is markedly greater. The difference between the various dilute acids lies not in their solvent power, which is similar for all, but in their influence on the adsorption process. The observed net effect of the acid on the soil is therefore expressed by the ordinary adsorption curve.

The reaction between dilute acids and soils thus appears to be essentially a displacement of absorbed material by something which is itself absorbed; and it falls into line with other displacements from colloids.

If this view is correct, it follows that acids need not be used in soil analysis, at any rate for the extraction of bases: any agent capable of being absorbed by the soil would serve equally well. Ramann has used a solution of ammonium nitrate and finds it dissolves at least as much potassium, calcium, etc., as an acid, and in some respects is more satisfactory. This method of extracting the bases from soils promises to be useful and to clear up many of the difficulties in soil analysis.

The water relationships of soils.

The earlier soil physicists, regarding soil as a mass of mineral matter, began their studies of the water relationships of soils by treating soil as a mass of sand, or, in mathematical analysis, of small bullets or marbles, and investigating the distribution of water by surface tension. The conclusions obtained were not wholly in accordance with facts. The facts observed in the evaporation of water from soil were particularly difficult to fit in with expectations, and numerous breaks in the curves seemed to indicate the existence of a variety of critical points and co-efficients. Keen has shown, however, that the phenomena become much clearer when regarded as colloidal effects. He found that the relationship of water to soil differs considerably from its relationship to sand. The evaporation of water from sand, silt, china-clay, and ignited soil proved to be relatively simple, and could be explained by the known laws of evaporation and diffusion. But the evaporation of water from soil could not: it was more complex. Instead of the simple proportionality between water content and time observed in the case of sand, the curves for soil were more exponential in type. The difference was traced to the soil colloids, and it disappeared when the soil was ignited and the colloidal properties lost: the curve then became identical with that obtained for sand. The influence of the colloids has so far only been expressed empirically, but it is

probably connected with the relation between vapour pressure and moisture content. But there is clearly something else at work, for the curve is not of a simple exponential type. It is necessary to allow for another factor: the effect on the rate of evaporation of the water surface in the soil, which obviously diminishes in area as evaporation continues.

The equation finally developed by Keen is:—

$$A\frac{dw}{dt} = \left(\sqrt[3]{\frac{ws}{100}} + 1\right)(\log_e(w + K) - \log_e K).$$

where $\frac{dw}{dt}$ = rate of evaporation.

w = percentage of water present by weight.
s = specific gravity of the soil.
A and K = constants.

This relationship holds without any break, proving that all the water in a normally moist soil is held in the same way without change in physical state. At one end of the curve the water is more easily given up than at the other, and in the competition for water between soil colloids and plants or micro-organisms some kind of equilibrium may be attained under definite conditions: this equilibrium is the "wilting point" of the physiologist. On this view the other constants and critical points that have been indicated by various investigators are all equilibrium points and do not represent breaks in the condition of water in the soil.

The retention of liquid water by soil, or, in other words, the resistance to drainage, is no doubt influenced by soil colloids. Attempts have been made by Alway and McDole to trace some connection between the amount of water absorbed by dry soil from a moist atmosphere and its water-holding capacity: in so far as these phenomena are related it is probably through their relationship to the soil colloids. The influence of salts on the permeability of soil to water, which is probably as much physical as chemical, has been studied by Hissink.

Soil Acidity.

It has long been known that some soils are acid to litmus paper, but become neutral on the addition of calcium carbonate. Acidity is not tolerated by most cultivated plants, and the agriculturist has therefore to guard carefully against it: the problem is one of high technical importance.

The older chemists took the obvious view that acidity was due to some special soil acid or acids, to which various names were given: humic acid, ulmic acid, crenic acid, apocrenic acid, etc. But no acid satisfying the modern chemist could be isolated, and when the colloid conception was introduced Cameron pointed out that the phenomena could all be explained as simple colloidal manifestations and did not require the assumption of soil acids at all. It was only necessary to suppose that the soil colloids absorbed the base more readily than the acid from blue litmus

and the whole phenomena are explained. In support of this view Cameron showed that cotton and other absorbents behaved exactly like " acid " soils, slowly turning blue litmus red; the phenomenon was therefore a general property of a class of absorbents.

Baumann and Gully applied this idea to the case of peat and showed that it fully explained all the known facts.

In the first instance they pointed out that it was not necessary to assume that the " acid " was a decomposition product because the original sphagnum was almost as " acid " as the peat.

Secondly, the acid if it exists must be insoluble because the water extract of the peat is practically neutral to litmus.

It must, however, be very potent because solutions of neutral salts such as calcium chloride, sodium nitrate, etc., are decomposed with liberation of free hydrochloric and nitric acids when treated with peat or sphagnum.

Baumann and Gully argue that no acid of this character is known to chemists, and it involves less strain to conceive of a physical adsorption of the base from the dissolved salt with liberation of the acid than to imagine an insoluble organic acid capable of decomposing simple salts in solution.

The view that acidity of the mineral acid soils is due to preferential absorption of the base was developed by Harris in an investigation of Michigan soils. The phenomena are substantially the same as for peat: the soil turns blue litmus red; an aqueous extract is neutral, while an extract made with a solution of a salt, *e.g.*, calcium nitrate, is acid. We must therefore assume either an insoluble but very potent mineral acid, or a preferential absorption of the base over the acid. The latter is indicated because, as in the case of peat, the amount of acid liberated from equivalent quantities of different salts is not the same, as it should be in a chemical reaction.

Daikuhara has applied this view to the case of the acid mineral soils of Japan and Korea, but he has modified the explanation and made it more easily intelligible to the chemist, who finds it difficult to understand why an unparalleled physical decomposition of a simple salt should be accepted, and the assumption of a difficultly soluble but potent acid rejected. Daikuhara shows that the development of the acidity in the salt solution is due to an exchange of bases and not to simple absorption of the base from the salt. If the acid solution is analysed it is found to be really a solution of an aluminium salt: aluminium being given up from the soil in amount approximately equivalent to the base absorbed. Aluminium salts, as is well known, turn blue litmus red, and therefore are indicated as acids. The phenomenon is still essentially an absorption, but the seat of the reaction is located.

This view is supported by Rice's experiments, which have demonstrated the substantial identity in hydrogen ion concentration of a solution of aluminium nitrate and the solution obtained by treating an " acid " soil with potassium nitrate solution.

Ramann adopts this view and gives up the expression "acid soils," using instead "absorptiv ungesättigte Boden." Kappen confirms the observations without entirely accepting the explanation.

The physical explanation of acidity has not passed unchallenged. Rindall of Helsingfors, Sven Odén of Upsala, Tacke and Ehrenberg have each argued in favour of definite humic acids in peat. Truog finds, in the case of mineral soils, that equivalent amounts of different bases are required to neutralise the acid properties of the soil—which, if generally true, would be easier to explain by assuming an acid than an adsorption.

It is always possible that both factors are at work. Evidence has been adduced by Christensen and by Schollenberger to show that acidity and base-absorbing power are not quite the same thing. Still more significant, measurements of the hydrogen ion concentration of soil extracts have been made, and show definite acidity.

Pan formation.

A pan is a layer of hard impermeable rock that gradually forms below the surface of the soil under certain conditions. Its effect is to cut off the soil above from the material below, and therefore to modify profoundly the movements of water and air, leading often to swampy conditions. The effect on vegetation becomes so marked that in agricultural practice the pan has to be removed, often at considerable trouble and expense.

The conditions determining the formation of pan seem to be a supply of organic matter, permeability of soil, low content of soluble mineral matter, and absence of calcium carbonate. These conditions occur most frequently on light sandy soils where, for some reason, the water is held sufficiently near the surface.

The older chemists explained the phenomena on purely chemical lines; it is unnecessary to go into the details of the various hypotheses put forward: in the main they involved alternate reductions and oxidations, or else solution in carbonic acid, and subsequent deposition. These hypotheses broke down on further examination, some necessary links failing to be realised when the experiment was made under natural conditions.

Recent workers, therefore (Munst, Ramann, Morison, Sothers, and Stremme), regard the whole process as a formation first of a "sol" and then of a "gel," and Morison and Sothers suggest the following as the most probable course of events.

It is well known that "sols" change to "gels" in presence of small quantities of electrolytes, and conversely "gels" often change to "sols" when electrolytes are removed. In normal soils the conditions are favourable to gel formation, but when in these particular soils the upper layer of sand becomes denuded of its soluble material by the persistent washing of rain water, the conditions become favourable for the formation of sols of ferric hydroxide and of humus—or ferric humate, if one likes to put it in that way. Morison and Sothers actually obtained such sols* by persistent washing of ferric-humus gels.

* As might be expected these did not give the ordinary iron reactions.

As the sol is washed down most of it passes to the permanent water level, where it remains and accumulates, diffusion being practically non-existent. During the dry months a certain amount of dessication takes place, involving a deposition of the sol as a gel: there is also a certain amount of transformation of sol to gel through the presence of electrolytes in the ground water.* Some of the humus gels become oxidised, some of both humus and ferric hydroxide gels change their colloidal properties in other ways. When wet weather comes on again it is no longer possible for the whole of the deposited gel to change back to a sol. Deposition has begun, and the place where this happened serves as a seat of further action.

This view seems more in accordance with the facts than the older one, in that it does not involve any unproved assumptions—such as reduction of ferric to ferrous iron and presence of ferrous iron in the pan.

Flocculation and Deflocculation.

Clay possesses well marked colloidal properties. If rubbed with water it becomes plastic, sticky and impervious: it shrinks on drying and absorbs heat: on moistening, however, the process is reversed and there is considerable swelling and evolution of heat. The importance of these observations is equally great in agriculture and in the ceramic industry.

Two hypotheses have been put forward to account for plasticity. Rohland attributes it to hydrated colloids present in the clay: Atterberg to minute flake-like particles which are able to slip over one another without difficulty.

Another property of clay is of great importance to agriculture, and has received much attention from agricultural chemists. Addition of a trace of electrolyte—acids or salts—to puddled clay causes considerable change in properties: the temporary loss of plasticity, impermeability and the power of remaining long suspended in water without settling; the clay is now said to be flocculated. The change can be watched if a small quantity of any flocculating substance is added to the turbid liquid obtained by shaking clay with water; the minute particles are then seen to unite to larger aggregates which settle, leaving the liquid clear. There is, however, no permanent change, deflocculation takes place, and the original properties return, as soon as the flocculating agent is washed away. Alkalies (caustic soda, caustic potash, ammonia and their carbonates) produce the reverse effect: they deflocculate clay, intensifying its stickiness and impermeability, and causing it to remain suspended in water for long periods.

These properties are of considerable importance in devising schemes of manuring for soils: it is obvious that alkaline substances are to be avoided on clay soil, however rich they might be in plant nutrients, as they would produce undesirable physical effects. On

* Ramann lays stress on this. Morison and Sothers do not because their sols were very stable in presence of electrolytes.

the other hand, slightly acid substances such as superphosphate have no bad effects, but rather the reverse.

Clay is thus an electro-negative colloid, its reaction probably being conditional by a trace of potash liberated by hydrolysis. It shows the general properties of electro-negative colloids as elucidated by Schulze and by Hardy: thus it is flocculated only by a solution containing ions or particles of opposite electrical valency and concentration of the ion. No quantitative relationships, however, could be found by Hall and Morison.

Pickering throws over the electrical hypothesis and attributes flocculation to a combination of the clay with the flocculant and the solute, whereby the aggregation of molecules increases so much that it loses its power of Brownian movement and soon settles.

Other effects of Colloids.

Various obscure changes are brought about on drying the soil. There is a marked increase in the proportion of water-soluble material, and, as Buddin has shown, in the ease with which nitrates are formed. Changes in the micro-organic population no doubt account for some, but not all, of these effects, and the simplest explanation is to attribute them to the changes in the colloids. Again, soil has a remarkable power of decomposing hydrogen peroxide, which is affected by small quantities of various substances, and may be a colloidal phenomenon. The decomposition of cyanamide in the soil has been attributed to colloids.

The influence of Colloids on Bacterial and Plant Life.

Plants and bacteria draw from the soil their water and their nutrient salts, and are therefore profoundly affected by anything that retards delivery of these essential substances. Inasmuch as colloids possess markedly absorbent powers they might serve as reservoirs to protect against loss by evaporation or leaching, or, on the other hand, they might actually compete against the plant and hold some of the supplies the plant ought to obtain.

As yet there is insufficient experimental evidence to show how the various factors are likely to interact. Fortunately, ecologists, both in this country and elsewhere, are fully alive to the possibilities: Gola has discussed the influence of the colloidal complex in determining plant habitats, and Söhngen its effects on the activities of micro-organisms; an illuminating résumé by Cavers has also appeared. It is interesting to note that soils destitute of colloidal properties are often infertile.

The Estimation of Soil Colloids.

Many efforts have been made to estimate the amount of colloidal matter in the soil. They fall into two groups based on the absorption of dye stuffs and of water vapour respectively. Methods based on the absorption of dye-stuffs have been elaborated by

Sjollema, Endell, Ashley, König, Hasenbäumer and Hassler, Hanley and Tadokoro, the last named giving other references also. Methods depending on the absorption of water vapour have been suggested by Mitscherlich. Different methods do not give altogether concordant results, nor is it to be expected that they should; it is highly improbable that any sharp dividing line exists in the soil between the typical colloids and the typical non-colloids; intermediate substances are to be expected showing colloidal properties only to a slight extent. It is certain, however, that the finer particles of the soil—the clay and fine silt—show much more marked colloidal properties than the coarser particles—the coarse silt and the sands.

The Constitution of the Soil.

Soil consists mainly of disintegrated and decomposed rock fragments of all sizes, varying from 1 mm. diameter downwards; these may be said to constitute its skeleton. Intimately mingled with these are the decaying remains of past vegetation. It seems necessary further to suppose that the particles are coated with a gel composed of silica, oxides of iron and aluminium, soluble organic matter, and a smaller quantity of lime, magnesia and potash, traces of ammonia, etc., this gel being spread relatively more thickly on the small particles than on the larger ones. This view of the constitution of the soil fits in with the known facts, and it has the further advantage of offering a definite starting point for further investigations.

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SEWAGE PURIFICATION WITH REFERENCE TO COLLOID CHEMISTRY.

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Although the problem of sewage purification, as it is known to-day, dates back to the introduction of the water-carriage system in the early part of the nineteenth century, the significance of colloid chemistry in relation thereto has only been observed within comparatively recent years.

Even at the present time, although certain theories have been elaborated with respect to the fate of the colloid matter during the purification process, in the main such theories have been established by analogy from the known characteristics of organic colloids and their behaviour under certain conditions rather than from any systematic study of the colloid matter actually present in sewage. So far as the writer is aware, no reliable data are available with respect to the separation, estimation and identification of the actual colloids present originally in the sewage and during the various stages of the purification process.

With the view, therefore, of indicating the present position in regard to the subject it is proposed (*a*) to state briefly the problem and (*b*) to give a résumé of the chief theories advanced with respect to the mechanism of the changes involved in the purification process, with special reference to the points of contact with colloid chemistry.

Briefly, ordinary domestic sewage may be said to be the water supply polluted by human excremental matter, kitchen and other domestic waste products. As in the majority of cases a combined drainage system is adopted, road detritus and washings must be added.

The character and strength of domestic sewage varies very considerably, dependent on the following factors:—

(i) The extent to which the water carriage system has been adopted.

(ii) The water consumption per head of population connected to the sewer.

(iii) Whether a combined, separate or partially separate system is in vogue.

(iv) Length of travel of outfall sewer.

(v) Rainfall, contour of district, nature of subsoil, and character of sewers, &c.

In industrial areas the character of the sewage is altered to an extent dependent on the nature and relative volume of the trade wastes admitted to the sewers.

In certain districts, *e.g.*, in woollen districts (Bradford, Huddersfield, &c.), or centres of chemical industry (Manchester, Birmingham, &c.), these are such as to alter very materially the character of the sewage, and consequently to vary the problem of its purification.

The main constituents of domestic sewage have been summarised by Fowler as follows:—

1. Matters in actual suspension:
   (*a*) Sedimentary matters, such as silt and sand, &c.
   (*b*) Floating and finely divided suspended matters (paper, rags, faeces, animal and vegetable debris, &c.).
2. Colloidal matters in pseudo solution or emulsion:
   Products of faecal emulsion, soaps and fatty matters, &c.
3. Matters in true solution:
   Ammonium salts resulting mainly from the hydrolysis of urea. Nitrogenous substances—urea, products of the decomposition of albumen—peptone-like bodies, carbohydrates; mineral salts—chiefly sodium chloride, with phosphates mainly derived from urine.

It will be understood that on account of its complex character and the unstable nature of its organic contents it is practically impossible to differentiate with anything like a high degree of accuracy the various states of the organic matter present in sewage which under physical and biological action is subject to transition from one form to the other.

O'Shaughnessy has shown that the colloid matter in pseudo solution is derived mainly from the faecal matter present, and that although there is a limit to the amount that can be taken up, the actual quantity (as measured by the 4 hours' oxygen absorption test) varies with the volume and character of the diluting water, the time of contact and the amount of agitation.

It is thus evident that the amount of organic "hydrosols" varies very considerably in different sewages. For an average domestic sewage it may be taken that roughly one-half of the soluble organic matter is present in pseudo solution.

Sewage is such a heterogeneous mixture of complex and varying character that apart from such determinations as chloride content, ammonium salts, organic nitrogen, total suspended and dissolved (true and pseudo solution) solids, its chemical examination is usually confined to certain empirical tests such as "albuminoid ammonia" resulting from the distillation of the sewage with an alkaline solution of permanganate of potash after removal of the ammonium salts,

which is taken as a measure of the albuminous bodies present, and "Oxygen absorption" from an acid solution of permanganate (usually $\frac{N}{80}$ K MnO_4) under stated conditions, which gives an indication of the amount of oxidisable matter present.

For the purpose of controlling purification plants, in addition to the above tests, the amount of oxidised nitrogen (Nitrite and Nitrate) is determined in the effluent.

Incubation will show whether the effluent is putrescible, and determination of the amount of dissolved oxygen absorbed by the effluent from aerated water, as recommended by the Royal Commission on Sewage Disposal as a Standard Test, will afford valuable information with respect to the matter still capable of fermentation, and consequently of the extent to which the oxidation change has been carried.

With the object of obtaining information in relation to what happens to the colloidal matters during the purification process, at any rate so far as the "hydrosols" are concerned, these tests have been supplemented by submitting the sewage and effluents to dialysis and thus determining the proportion of dialysable to non-dialysable matter and their respective oxygen absorption and albuminoid ammonia content, *see* Rivers Committee Report, Manchester, 1901, Kröhnke & Biltz, Fowler & Ardern, Travis & Johnston, O'Shaughnessy & Kinnersley (1901–1906).

An objectionable feature of this method of attack is the time required by the dialysis operation, which is usually not less than 24 hours, even where the determination is stopped when equilibrium is attained (as measured by the chloride content) on either side of the membrane employed, during which period there are many possibilities of change of character in an unstable liquid like sewage. In the method employed by Johnston for the complete separation of the non-dialysable from the dialysable constituents of the sewage, a period of 6 days usually elapsed. The sewage and effluents were sterilised by the addition of acid with the idea of obviating changes due to bacterial action, but it is obvious that mere acidification is likely to alter the character of the samples under examination.

The method proposed by Rübner of coagulating the colloidal matter by precipitation with acetate of iron surmounts this difficulty but introduces other errors with respect to the removal of organic matters in true solution. Fowler and others elaborated this test and called it the "clarification test," while Rolants compared the effect of acetate of iron with that of calcium chloride and sodium phosphate, alumina, and powdered talc, respectively, the latter material being employed with the idea of avoiding precipitation of organic matter from crystalloidal solution.

A difficulty common to both these methods of investigation is the character of the preliminary treatment of the sample, undertaken for the removal of the finely divided non-colloidal matter. The method of procedure is either to allow the sample to stand

for a stated period and to work with the supernatant liquid, or to filter the original sample through filter paper. The first procedure is open to the objection that matters in what may be termed 'macroscopical' suspension are incompletely removed, while filtration through paper, in addition to the removal of such matter, may also remove actual colloids by the absorptive action of the film of suspended matters formed on the filter paper. It will thus be seen that it is difficult to differentiate between particulate suspended matter in a state of fine division and actual colloidal matter.

The object of sewage purification is primarily to obtain an effluent which will not pollute the water course into which it is discharged.

An effluent may be said to be entirely satisfactory which avoids the following:—

1. Secondary decomposition which may give rise to aerial nuisance.
2. Deaeration of the body of water into which it is discharged.
3. Deposition on the bed of the watercourse.

Having regard to the conditions usual in this country of the relative volumes of the stream and sewage, the production of such an effluent involves the removal of suspended matters and of the putrescible organic matter in colloidal and crystalloidal solution.

In the following paragraphs is given a brief account of the methods generally adopted to effect this object.

The sewage as it arrives at the outfall works is usually passed through a detritus and screening chamber, where the heavier sedimentary matters, road detritus, &c., are removed, together with floating matters, such as rags, paper, &c., and a proportion of the non-disintegrated faecal matter.

Apart from the treatment of sewage on land by broad irrigation, or in some cases of intermittent filtration, or by the activated sludge process, which will be briefly considered later, the screened sewage then receives preliminary treatment by one of the following alternate methods:—

1. Plain sedimentation tanks.
2. Chemical precipitation tanks.
3. Specially designed tanks such as the Hampton (Hydrolytic) or Emscher tank.
4. Specially constructed contact beds, such as the Dibdin slate filter.

The main object of this preliminary treatment is to remove, as far as possible, the actual suspended matters in order to facilitate the subsequent filtration of the sewage.

In septic tank treatment, anaerobic fermentation of the sewage is encouraged, with the view of reducing the volume of sludge to be dealt with, while the double-decked tanks of Travis (Hampton) and Imhoff (Emscher) are designed to confine such anaerobic action to the deposited sludge and so avoid a septic effluent.

Except in special cases where the sewage itself contains trade waste which may coagulate colloidal matter, simple sedimentation of the sewage, while doubtless effecting removal of a considerable proportion of the organic colloidal matter in the ' gel ' form, is practically without effect on that in the ' hydrosol ' condition.

A certain proportion of the ' hydrosols ' will be carried down by chemical treatment, but unless a fairly heavy dose of salts of iron or alumina with or without lime is employed, when the process becomes expensive and in many cases impracticable, the tank effluent still contains appreciable quantities of organic colloidal matter.

Kröhnke and Biltz, Rolants and others have shown that in the main the sewage colloids possess a negative charge which very probably is not without effect in regard to the value of the salts of trivalent metals of opposite charge, such as those of iron and alumina, in coagulating the colloidal matter present in sewage. The purely chemical reactions and the effect of the extended surface afforded by the precipitate formed, cannot, however, be neglected in considering the process of chemical precipitation.

While considering this question, mention should be made of the suggestion of Rohlands to use plastic clay as a means of separation of colloid matter. Polz, however, reports that as the result of large scale trials with dyeworks effluent, the process is both unsatisfactory and impracticable.

Reference should also be made to Degener, who, arguing by analogy from the absorptive action of the ' humus ' in soil, worked out a method of purifying sewage by precipitation with powdered lignite and iron salts, which it is claimed is capable of removing not only the suspended solids, but also the colloid and other putrescible matters in the sewage to the extent of producing a non-putrescible effluent. Dunbar, however, reports that it is only applicable in certain special cases, and that its cost is too great for general adoption.

Effluents from ordinary septic tanks usually contain appreciably more finely divided suspended matter than the effluent resulting from either chemical treatment or simple sedimentation, as the result of the constant rising and falling of particles of sludge due to the gas evolved consequent on the anaerobic decomposition of the deposited sludge.

It has been found generally that as a result of septic treatment there is a small though appreciable reduction in the amount of oxidisable matter in true solution.

With regard to the action on the matter in pseudo solution, this seems to vary with the character of the sewage treated with particular reference to its original colloid content.

O'Shaughnessy, working with a mixed trade sewage of low colloidal content, concluded there was a slight increase in the oxidisable matter in pseudo solution as the result of treatment in septic tanks, and Fowler and others have stated that where septic action was vigorous as the result of higher temperature there is evidence of some slight increase.

On the other hand Rolants, employing a precipitation method for removal of colloids, found that while the percentage of the total oxidisable matter present in pseudo solution was slightly higher in septic tank effluent than in the sewage treated, the actual amount of colloidal matter (as measured by the permanganate test) was, if anything, rather less. On determining the organic nitrogen and organic carbon contained in the colloids present, which was considered to give a better appreciation of the colloid matter than does the oxygen absorption test, he found in every case a diminution of colloid matter in the septic tank effluent as compared with the original sewage.

On the whole, it may be considered that septic action as exhibited during septic tank treatment has no material effect on the amount of matter in pseudo solution, the differences found being very little more, if any, than the errors in the method of estimation.

The chief object of preliminary treatment in slate beds is to keep the solids deposited therein under aerobic conditions as far as possible, and Dibdin has shown that if operated in a proper manner a considerable destruction of the deposited sludge is brought about by the agency of bacteria, moulds, and higher organisms, such as protozoa, worms, &c.

While it is possible that contact with the slates will tend to flocculate, by surface action, some of the matter in pseudo solution, the filters are too open to be very effective in this respect, and it is understood that the effluents obtained are still turbid and contain appreciable quantities of colloidal matters.

It can be stated that with properly designed plant, having regard to the maximum permissible velocity of flow, a more or less complete removal of the grosser suspended solids can be obtained, and that, dependent on the character of the sewage, a considerable proportion of the more finely divided solids, including, doubtless, colloids in the ' gel ' condition, may be effected.

It is, however, evident that none of these preliminary processes, except heavy chemical treatment, affect appreciably the organic matter in pseudo solution.

The resultant effluent, therefore, contains practically the original sewage solids in solution together with a varying proportion of the finely divided suspended solids, and its subsequent purification involves the application of extended surfaces.

This is usually effected by distribution on land or on artificial filters composed of various inert media of different grades, in which the liquid is held in contact with the filtering media (placed in water-tight tanks), or is allowed to percolate through, either intermittently or continuously.

Briefly, it may be said by the adoption of any of these methods no difficulty need be experienced in obtaining a satisfactory effluent, provided due attention is paid to the design of the purification works and to its capacity in relation to the volume and character of sewage treated.

With the object of dealing with the mechanism of the complex changes, physical, chemical and biological, which take place during

the oxidation or purification process, it is proposed to consider briefly the three main theories which have been advanced in explanation of the purification phenomena, more particularly with reference to the fate of the colloid matter.

The earliest theory advanced with respect to the mechanism of the purification changes effected by the filtration of ' sewage ' was based on the work carried out at the Lawrence Experimental Station, Mass., in respect of the development of the intermittent sand filters as advocated by Frankland, as a practical means of sewage purification.

According to this theory, the suspended solids applied with the sewage or tank effluent are arrested mechanically in the filter by virtue of its fine pores, and subsequently oxidised, and the organic matter in solution is directly oxidised and mineralised by bacterial agency during the course of its passage through the filter with the accumulation within the filter of small quantities of ' humus,' which is very resistant to further fermentation. Presumably colloids are included in the organic matters in solution, although they are not referred to specifically.

This simple representation of the purification process received almost universal support, notably by Stoddart as recently as 1909.

Dunbar assumed that it was not possible to bring about the complete oxidation of the complex organic matter present in solution in sewage during the short period of time taken by the liquid in passing through the filter, and as the result of a series of experiments extending over a considerable period (1897–1900) carried out by him and his colleagues at the Hamburg Hygienic Institute (*vide* ' Principles of Sewage Treatment ') he advanced what is known as the " absorption theory " of sewage purification.

This theory explains the mechanism of the purification changes as follows:—

1. The actual suspended matters are removed by attraction of the filtering media, &c.
2. The dissolved matters (true and pseudo solution) are retained by absorption phenomena, which is accelerated and increased as the slimy matter, or what is termed the bacterial film, accumulates on the media as the filter becomes mature.
3. That the matters thus retained are oxidised by chemical action (condensed oxygen, &c.), and by the agency of bacteria and higher forms of life. The resultant soluble products—mineral salts, amino-acids, &c.—are subsequently washed out of the filter by succeeding quantities of sewage treated.
4. That this absorption process is prevented from ceasing by the action of micro-organisms, &c., in the presence of atmospheric oxygen.
5. There is a residue of organic matter, &c., which is very resistant to further oxidation changes, which either accumulates in the filter or is discharged with the effluent.

It will be noted that this theory draws no distinction between matters in true and pseudo solution so far as the mechanism of the purification changes is concerned.

Experience with the operation of the Hampton sewage works, where relatively large quantities of sludge accumulated in the filtration area, led Travis to study the question of sewage colloids in relation to sludge production. As the result of a series of experiments carried out in conjunction with Johnston, he advanced in 1905 what is known as the Hampton Doctrine.

According to this theory the purification process is primarily and essentially a de-solution effect brought about purely by physical causes and that any bacterial or biological action is definitely ancillary.

Unlike Dunbar's theory, a distinction is drawn with regard to the mechanism of the purification process as between organic matter in colloidal solution and matter in true solution.

It is held that whereas ' organic matters and products in actual solution, *e.g.*, ammonia, sulphuretted hydrogen and volatile products, are absorbed by the accumulated deposits in the filter,' the solids in colloid solution are coagulated or precipitated ' in virtue of a physical action '—effect of extended surface contact, &c.

These coagulated colloids are either retained in the filter or discharged with the effluent from the filter, and any biolytic action on them is a very slow and prolonged process, and consequently in addition to the actual suspended solids in the sewage or tank-effluent treated, the amount of such coagulated colloids which have been termed ' ultra sludge,' must receive attention in considering the amount of the total sludge to be dealt with.

In discussing these theories, it is proposed to confine attention as far as possible to the purification effect on matters in colloidal solution.

Briefly, it may be said that—

(i) In the earlier theory, especially as propounded by Stoddart, that such matters are held to be oxidised directly by bacterial agency during the passage of the liquid through the filter.

(ii) That Dunbar's theory provides for their preliminary absorption by the filtering media and the gelatinous coating thereon, with subsequent more or less rapid oxidation by agency of condensed oxygen, bacteria and higher forms of life.

(iii) That according to the Hampton Doctrine, such absorptive processes are confined to the matters in true solution, and that the matter in pseudo solution is coagulated by virtue of a physical action. That the subsequent biolytic oxidation of the matter thus deposited is a very prolonged process.

In connection with the question of absorption, it may be mentioned that Clark, and later Clifford, have demonstrated that the mean time of passage of sewage through a filter as operated in practice, while it varies considerably, dependent on several

factors, is on the whole, much longer than the few minutes spoken of by Dunbar, and may in some cases amount to more than one hour, which would allow time for appreciable bacterial action.

Also that Harriette Chick, Fowler and Gaunt, and Stoddart have shown that absorption of ammonium salts does not take place under sterile conditions except with material such as clinker, &c., which allows of chemical interaction between the liquid and the media. Stoddart has extended this observation to solutions of albumen and was unable to confirm Dunbar's experiment which shewed 50 per cent. loss of albumen. He suggests either preliminary decomposition (prior to use) with formation of ammonia which would be partially fixed by the clinker, or direct chemical interaction as a possible explanation. It is obvious that experiments designed to shew purely absorptive phenomena should be carried out with material entirely inert, such as pure quartz as used by Fowler and Gaunt.

Stoddart's conclusion that there is no evidence of the preliminary absorption of the soluble constituents of sewage was based on the results of his experiments on the nitrification of solutions of (*a*) ammonium salts (*b*) urea (*c*) albumen and (*d*) of sewage deprived of its suspended matter by filtration through paper, in which the flow through his experimental filter (seeded with a vigorous growth of nitrifying organisms) was interrupted from time to time, and the liquid treated replaced by salt solution of known strength applied at exactly the same rate.

The coincidence of a series of curves plotted with respect to the time taken to attain maximum nitrification and maximum chloride content was claimed to establish that preliminary absorption did not take place.

Stoddart also objects to the absorption theory, developed as it was as the result of studies with contact beds, being applied to the modern percolating filters where the conditions differ very considerably. On the other hand, Dunbar considers that such altered conditions are more favourable to absorptive phenomena.

For a full discussion of the difference between the theory of preliminary absorption of colloidal matter and of its direct coagulation and deposition in the filter, the reader is referred to a paper presented by Travis to the meeting of the Association of Managers of Sewage Disposal Works at Leicester (July 4th, 1908), which appeared in the July 10th, 1908, issue of the *Surveyor*, and to the discussion thereon which ensued between the author and Lübbert, of the Hamburg Hygienic Institute.

So far as the mechanism of the preliminary removal of the matter in colloidal solutions is concerned, both Dunbar and Travis agree that it is essentially the result of physical action; mention should therefore be made of the work of Fowler and Mumford. They found that under strictly aerobic conditions, a bacterium isolated from a body of water receiving colliery discharges, acting through its enzyme in the presence of small quantities of iron salts, was capable of coagulating sewage colloids in the course of a few hours. Such removal of colloid matter from pseudo-solution is effected without the aid of surface content other than is provided by the air bubbles and the matter precipitated.

The evidence available with respect to the mechanism of the removal from sewage of organic matter in pseudo-solution may be summarised thus:—

(i) The experiments of Stoddart designed to show its direct oxidation by bacterial agency cannot be considered conclusive. On the other hand it has not been demonstrated that under the favourable conditions present in an efficient filter, in which the sewage passes in thin films over a network of media covered with an active bacterial slime, the mean time of passage is insufficient to allow of direct biolytical oxidation of some portions of the organic matter in pseudo-solution.

(ii) While it is accepted that sewage colloids may be precipitated or coagulated by intimate surface contact, this 'de-solution' theory can scarcely represent the whole phenomena of colloid removal otherwise such action would continue in the absence of micro-organisms.

(iii) The conditions met with in a mature and efficient filter are such as to render it most probable that absorption phenomena play an important part in the removal of matters from pseudo-solution.

In considering the final fate of the matters removed from pseudo-solution during the purification process it may be said that, independent of what may occur with experimental filters inoculated with vigorous growths of micro-organisms, and operated under ideal conditions, Stoddart's view that none of the solid matter retained in sewage filters is derived from organic matters originally in pseudo-solution is not consistent with what obtains in actual practice.

On the other hand, the contention of Travis that the retained colloids undergo very little change as the result of biolytic action was formulated on entirely inconclusive evidence.

In this connection mention may be made of Dunbar's experiment in which a solution of albumen containing nitrogen equivalent to the organic nitrogen content of an average sewage was applied to a mature filter, with the result that almost quantitative oxidation of the sulphur was obtained, while 58 per cent of the total nitrogen appeared in the filtrate, 10 per cent. as ammonia, 20 per cent. as nitrate and 25 per cent. as organic nitrogen. Thus 42 per cent. of the nitrogen disappeared either in the gaseous form or accumulated in the 'humus.' A considerable part of the carbon of the albumen also disappeared as gaseous carbonic acid, but a part also went to form the 'humus' which accumulated in the filters.

The Massachusetts intermittent sand filters have demonstrated that the amount of retained nitrogenous matter after 18 years' continuous operation with 'regulation station' sewage containing its original suspended solids only amounts to from 4 to 5 per cent. of the total nitrogen in the sewage applied. Travis estimates this to be equal to about 20 per cent. of the original organic nitrogen.

Recently, Clark in reporting on these filters after they had been at work for 28 years, states that for some years only as much sewage has been applied as can be purified without increasing the amount of organic matter stored in the filters.

Comparison of the conditions obtaining in these filters with those of the modern ' artificial ' filters in which sewage is treated at very much higher rates, leads to the conclusion that the results obtained may certainly be considered a maximum effect with respect to the resolution of the organic matter deposited in the filter, at any rate so far as any practicable scheme of sewage filtration is concerned.

The fact that the sewage treated contained its original solids in suspension unfortunately precludes any definite conclusion with regard to the actual resolution of the solids derived from matters in pseudo-solution.

In the Second Annual Report of the State Department of Health of Massachusetts (1916), Clark reports the results obtained with the operation of a series of sand filters receiving respectively, (*a*) untreated sewage, (*b*) settled sewage, (*c*) sewage after treatment in straining filter, and (*d*) sewage clarified by precipitation with sulphate of alumina. The volume of sewage applied to each filter was varied so that each received as nearly as possible equal amounts of organic matter (measured by the organic nitrogen). It is interesting to observe that working in this manner there was no material difference in the amount of nitrogenous matter stored in the respective filters, measured by determining the amount of albuminoid ammonia in the sand.

It would thus appear that the nitrogenous organic constituents of sewage whether in actual suspension or in colloidal solution are more or less equally amenable to biolytic action, and consequently the percentage resolution of total organic matter observed in connection with the sand filters treating crude sewage should apply fairly well to the matters coagulated from pseudo-solution.

In conclusion it is evident that the total unresolved organic matter either retained in the filter or discharged with the effluent, will depend on the character (suspended solids and colloid contents) of the sewage treated and the rate of application with respect to the capacity of the filter, which will vary according to the type employed.

A survey of the subject would not be complete without reference to the large scale operations developed by O'Shaughnessy with reference to the subsequent treatment of the sludge removed from the Birmingham sewage by treatment in sedimentation on septic tanks.

This sludge is submitted to prolonged anaerobic fermentation, whereby appreciable auto-digestion of the sludge occurs with loss of colloidal character. By this treatment a dense and granular material is produced without nuisance. (*Vide* Reference, 1914, J.S.C.I., No. 1, vol. xxxiii.)

The following reference to the " Activated Sludge " process of sewage purification is made on account of the rapid removal of oxidisable matter in pseudo-solution, which is effected without the aid of actual surfaces, other than is provided by the particles of sludge.

An " active " sludge is built up as the result of the oxidation by aeration of successive quantities of screened and detritus free sewage.

This sludge is flocculent in character, has a very high bacterial content and contains numerous higher forms of life especially ciliated protozoa.

When sewage is aerated in intimate contact with from 20 to 25 per cent. (by volume) of activated sludge, there is a rapid initial removal of oxidisable matter from pseudo-solution, with the production of a well clarified effluent, which is nitrified on further aeration.

Judging by the volume of sludge produced it is presumed that the colloidal matters are removed from solution either by the absorptive action of the flocculent sludge or coagulated by intimate contact with the sludge particles, or as the result of enzymic action.

While Bartow has shown that large quantities of carbonic acid are produced during the purification process, which is indicative of vigorous biolytic action, the high proportion of organic matter in the resultant sludge appears to preclude any material destruction or resolution of the organic matter present in the original sewage either in actual suspension or in colloidal solution although it is evident from its appearance there has been a considerable alteration in its physical character.

The high nitrogen content of activated sludge, which varies from 4 to 7 per cent. (dry matter) dependent on the character of the sewage treated, leads to the same conclusion, as Clark has shown that the sewage colloids contain much more nitrogen than do the grosser suspended solids.

There is, however, an undetermined factor, viz.:—to what extent, if any, is there any fixation of atmospheric nitrogen?

Ardern and Lockett have studied this question, but further information is required before any definite pronouncement can be made.

As previously stated, the sludge is quite flocculent and readily separates out from the purified sewage.

Presumably on account of its gelatinous condition, the water content of the sludge is very high and cannot be reduced below 95 per cent. by simple sedimentation.

When this percentage has been reduced to from 88 to 90 per cent., either by centrifuge, or by treatment on drainage filters, the sludge is of the consistency of a fairly stiff jelly, whereas ordinary sludge obtained from the sedimentation of sewage, containing a similar amount of water, is quite fluid and can be readily carried and discharged through pipes.

The solution of the problem of the best means of preliminary de-watering of this sludge, prior to drying, involves a study of the conditions favourable to the removal of water retained by colloids in the "gel" state.

Chalkley Hatton has shown that such de-watering can be effected by treatment in a modified type of filter press, with the production of a cake containing 75 to 80 per cent. moisture.

There is, however, room for research, with special reference to electrical effects, in regard to the most economical method of de-waterising and drying the sludge.

The problem is one of considerable importance to agriculture, involving as it does the utilisation of the full value of the sludge as a fertiliser.

A complete bibliography of the activated sludge process will be found in Porter's publication given in the list of references submitted.

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COLLOID PROBLEMS IN DAIRY CHEMISTRY.

(Milk, Butter, Cheese, Margarine, and Ice-cream.)

By WILLIAM CLAYTON, M.Sc., *Chief Chemist, Calders Margarine Co., Liverpool.*

In this paper it is proposed to treat of Dairy Chemistry under special headings, drawing particular attention to the colloid phenomena and problems involved. Milk (the basis of all the other products), butter, cheese, margarine, and ice-cream, each receive special consideration:—

MILK.

Milk contains substances which are inherently colloidal in nature, *e.g.*, casein and albumen, and also materials which behave as colloidal systems by virtue of their fine state of subdivision, *e.g.*, the fat present as emulsion, the cell-content of milk, and the enzymes of milk.

The casein of milk, a protein combined with phosphates of the alkaline earths, is present to the extent of about 3 per cent., whilst the second protein body, albumin, is present to about 0·5 per cent. Casein is so important from the standpoint of the colloid chemistry of milk, that a separate section of the paper has been devoted to it. The albumin, known as lact-albumin, is separated from casein, by precipitating the latter with acetic acid. Pure lact-albumin is an amorphous, tasteless powder. In aqueous solution it is coagulated by heating to 70° C., but only about 85 per cent. to 90 per cent. is thus precipitated. [*See* Rupps. U.S. *Dept. Agri. Bureau of Animal, Ind. Bull.* 166. Pp. 1-15. (April, 1913).] Lact-albumin is soluble in saturated aqueous Mg SO_4, but is precipitated if acetic acid be added. A crystalline form of this albumin is obtained if the saturated Mg SO_4 solution has an equal volume of water added, a little acetic acid being present, and then allowed to stand.

Amongst other reactions given by the albumin proteins, lact-albumin is thrown out of solution by saturation with ammonium sulphate, or by addition of tannin, or phosphotungstic acid. It is insoluble in alcohol.

Some evidence has been obtained for the existence in milk of a third protein, lacto-globulin, present to the extent of about 0·15 per cent. It is soluble in acidified NaCl solutions, is coagulated at 72° C., is not coagulated by rennet, and is precipitated by sodium sulphate, and tannin.

See { Hammarsten, *Z. f. physiol Chemie*, **8**, 467 (1183-4).
Sebelien, *Z. f. physiol. Chemie*, **9**, 445 (1885).
Schlossmann, *Z. f. physiol. Chemie*, **22**, 197 (1896).

The colloid chemistry of milk chiefly centres round the phenomenon of "protection," in this case, the protective action exerted by lact-albumin on casein. The subject has been well investigated, and is fairly involved; for its complete understanding, the compositions of various milks must be studied. The following table of

the average composition of various milks is Leach's compilation from Koenig's, "Chemie der mensch-Nahrung und Genussmittel."

Constant.	*Cow.*	*Human.*	*Goat.*	*Ewe.*	*Mare.*	*Ass.*
S.G.	1·0316	1·03	1·0305	1·0298	1·0347	1·036
Water per cent.	87·27	87·41	85·71	80·82	90·78	89·64
Casein.	3·02	1·03	3·20	4·97	1·24	0·67
Albumen.	0·53	1·26	1·09	1·55	0·75	1·55
Fat.	3·64	3·78	4·78	6·86	1·21	1·64
Milk Sugar.	4·88	6·21	4·46	4·91	5·67	5·99
Ash.	0·71	0·31	0·76	0·89	0·35	0·51

It has long been known that infants can digest human and asses' milk more easily than cows' milk cf. Jacobi, *Journ. Am. Med. Assocn.* **51**, 1216-1219 (1908). "Asses' milk has always been recognised as a refuge in digestive disorders, when neither mothers' or cows' milk, or its mixtures, were tolerated."

From the above table we see that in cows' milk the ratio of albumen to casein is only 0·53 to 3·02, whereas in human milk it is 1·26 to 1·03, and in asses' milk 1·55 to 0·67 (or over double the amount). "In cows' milk the casein forms 5/6ths of the total proteids in the milk, whereas in women's milk the casein forms 2/6ths of the total proteids." (Koplik, "*Diseases of Infancy & Childhood*," 1902.)

Human milk is hardly curdled at all by acid or rennin, the reverse being true with cows' milk. We see then, that the ratio of protective colloid (albumen) to the irreversible coagulative colloid (casein) is a most important factor.

"Cows' milk precipitates or coagulates very early with the aid of acids or salts; women's milk quite late or not at all. Hence in the infant stomach, cows' milk does not take up much acid of the gastric juice and soon coagulates in large masses. Women's milk, on the other hand, takes up a large amount of acid of the gastric juice, and coagulates late in small masses. The differences in the modes of coagulation in the two caseins are of great importance in the study of infant feeding." (Koplik, *loc. cit.*)

Cows' milk can be made to resemble human or asses' milk in protective qualities by the addition of such colloidal substances as gelatine, gum-arabic, cereal gruel, or barley water (a starchy solution). Very interesting observations with the ultra-microscope were made by Alexander and Bullowa on this subject:—*see Chem. News*, **101**, 193 (1910). These authors followed the coagulation of milk by heat, rennin, and acids, with and without the addition of protective colloids, by the aid of the ultra-microscope. They concluded that "the casein of milk is an irreversible or coagulating or unstable colloid, which is protected by lact-albumen, a reversible or stable colloid," and further that "in the modification of cows' milk for infant feeding, it is necessary not only to consider the per cent. of total proteids, fat, etc., present but to see that the casein is adequately protected." (*Loc. cit.*, p. 195.)

The fat present in milk is carried down by the curd resultant upon milk-curdling. The greater the extent of coagulation, the larger is the amount of fat carried down with the curd, and since such fatty curds tend to coalesce and give rise to large masses little amenable to the action of the digestive juices, it follows that

protection of the casein by some agent such as albumen or gelatine is most advantageous.

cf. Alexander, *J. Am. Chem. Soc.* **32**, 680–87 (1910).
Auzol, *These de Paris* (1907).
U.S. Pub. Health and Mar. Hosp. Serv., Washington, Hyg. Lab. Bull. **41**, p. 658.

A most interesting and comprehensive study of "The Coagulation of Cows' Milk in the Human Stomach" has been made by Brennemann (*Arch. Pediatrics* **34**, 81-117 (1917)).

He found that when fresh milk is drunk, the curds formed in the stomach are very large and hard, whilst milk boiled for 5 minutes gives rise to small soft curds. The curds become harder and bigger as the fat content of the milk is decreased. An increased fat content leads to smaller and softer curds, but their digestion is less rapid. A rapid ingestion of milk produces larger curds than does the sipping of milk.

Diluted milk leads to finer, flakier, and more porous curds. Lime water and milk do not easily coagulate, even if at all. Barley water and other starchy decoctions, when added to the milk, lead to smaller curds, more easily digested; they exert a "protective" influence over the casein.

Another phenomenon of great interest in colloid chemistry is exhibited when milk is boiled, or made into milk puddings, etc., namely, the formation of a skin or membrane at the surface. This subject has been investigated by Ramsden:—

Archi. f. Anat. u. Physiol., pp. 517–534 (1894).
Proc. Roy. Soc. **72**, 156–164 (1903).
Zeit. phys. Chem. **47**, 336 (1904).

Ramsden asserts that for this membrane formation there must be present a free (gas) surface, and a general system as follows:—

water ⌐——⌙ dissolved colloid ⌐——⌙ gas.

Particles of the dissolved colloid passing spontaneously out of the solution give rise to a delicate surface pellicle or membrane. Ramsden found that all albumins in time can form such a skin at the still surface of their solutions. The colloid lowers the surface tension of the liquid and passes into the surface layer (adsorption), the process being an irreversible one. Even dilute solutions can yield a highly concentrated surface layer, following definite mathematical relations; *see* Milner (*Phil. Mag.* 1907 (vi) **13**, 96).

The Fat in Milk Cream.

Milk contains about 3·6 per cent. of fat, present as an emulsion of fair stability. On standing, the greater portion of the fat rises to the surface, as cream, and the milk then contains about 0·2 per cent. fat (water = 90·4 per cent.). Much argument has taken place as to whether the fat globules in milk are surrounded by a membrane, or by a gelatinous mucoid substance, semi-liquid, usually referred to under the Danish name "slim-membran." Storch claims to isolate this mucoid body by treating cream until all the lactose, casein, etc., has been washed away. Staining milk with ammoniacal picrocarmine, Storch examined the fat globules under the microscope and observed a stain layer enveloping each globule. Though he claims

this fact as additional evidence for his " slim membran " theory, the modern notion of adsorption can account for such staining without assuming a mucoid surface at all.

A milk from which the cream has been separated may be used as the medium for emulsifying such oils as coconut oil, and cotton-seed oil, to yield artificial milks, emulsions of great stability. Such a result decidedly tends to disprove the notion of a mucoid substance being necessary for the existence of the fat in milk as small globules.

Cream is formed by the rising of the fat globules through the denser milk serum to the surface. The density of the liquefied fat is about 0·92, whilst that of the milk serum is over unity. The diameters of the fat globules vary between 0·01 mm. and 0·0016 mm. Thick cream contains about 56 per cent fat, and 39 per cent. water, whilst thin cream contains about 29 per cent. fat and 64 per cent. water. The fat content varies between very wide limits, and the percentage of fat is in inverse ratio to the density of the cream.

The purchase of cream is based on its thickness, which is usually measured by its viscosity. Thickness is often induced by the aid of such substances as gum tragacanth, gelatine, starch, " viscogen " (lime and sucrose syrup), or by the process of homogenising, *i.e.*, forcing the cream through minute orifices (at a suitable temperature below 60° C.) under pressure. (*See* section on homogenised milk.)

Since it is impossible to whip cream which has undergone homogenisation, gelatine, agar-agar, or gum tragacanth is added to the extent of about 0·1 per cent., so as to induce permanent frothing on beating up the cream. It is interesting to note that homogenised cream cannot be churned into butter.

Butter.

When milk or cream is churned, the globules of fat coalesce and granules are formed, which are then worked together to give a mass of apparently homogeneous texture. The average fat content of butter is 83·5 per cent. fat and the water content about 13 per cent. When examined under the microscope with crossed Nicol prisms, a uniformly dark field is viewed, whereas margarine under similar conditions presents a dark field containing bright portions and indistinct crystalline structures. The fat in milk, on churning into butter, has no crystalline structure, whilst margarine fats have, owing to their repeated melting and cooling.

As to the exact changes occurring when milk fat is churned into butter, there is still divergence of opinions. The upholders of the " slim-membran " theory, argue that the mucoid substance enveloping the fat globules is rubbed off, and the globules thereupon coalesce. Fleischmann inclines to regard the process of churning as being the solidification of superfused fat globules, but this theory is discredited by the fact that the fat-globules in milk are rapidly solidified by mere cooling.

It is very likely, however, that there is an adsorption layer of some kind around the fat, and that during churning this layer is continually thinned out by the impacts of the various globules, eventually permitting coalescence to small nuclei, which grow by

degrees until that particular moment arrives when the butter particles suddenly become visible. There is still room for considerable physico-chemical research in connection with this long-known but little-elucidated phenomenon.

The butter nuclei are worked up to a homogeneous mass, which the microscope shows to be a solid emulsion of fat, with fat the continuous medium, and water the disperse phase, an exact reverse of the system occurring in milk. (Compare section on "Margarine.")

The physical conditions of churning, especially the temperature, exert a profound influence on the butter, particularly with regard to its moisture content. The main factors to be considered in this connection are the fat content, the acidity, and the viscosity of the cream, and the agitation employed. A cream containing 30 to 45 per cent. of fat churned at a temperature ranging from 13° C. to 18° C. should give good results. As cream ripens, lactic acid is produced, the viscosity of the cream diminishes, and churning becomes easier. In this connection it is interesting to note that acids tend to make emulsions "break," *i.e.*, separate into oil and water, probably by some action on the protective (emulsifying) agent present. Here the casein is coagulated and precipitated if the acidity is too pronounced, and casein clots may be found in the butter mass. Churning must not be conducted too rapidly and violently, for then the moisture content will be too high owing to the enclosure of buttermilk within the nuclei. Also churning must be stopped as soon as the butter granules reach the size of small peas, otherwise the granules will coalesce and retain an excess of buttermilk which cannot be washed out again.

The physical chemistry of butter as a solid emulsion has been little studied, as indeed have any cases of solid emulsions, a matter which is referred to in more detail when discussing "Margarine."

Casein.

Casein is a phosphoprotein occurring to the extent of about 3 per cent. in cows' milk and about 1 per cent. in human milk. It is combined with the phosphates of the alkaline earths yielding a pseudo-solution or very fine colloidal suspension. Some writers adopt Halliburton's nomenclature and use the name "caseinogen," reserving the term "casein" for the curd produced by the action of rennet on milk. In this paper the term "casein" is used throughout (following Hammarsten).

Casein is precipitated from milk by saturating with NaCl, MgSO4, $(NH_4)_2SO_4$, and mineral acids; also by tannin, metaphosphoric acid, phosphotungstic acid, $CuSO_4$, $ZnSO_4$ and by rennet. It is soluble in alkalies and in solutions of salts which hydrolyse to alkaline solutions, *e.g.*, phosphates, and it is insoluble in alcohol and ether.

When pure, casein is a white amorphous, odourless, tasteless solid soluble in water to about 0·1 per cent. Though precipitated by mineral acids, it redissolves in excess of acid. Opalescent solutions are obtained when casein is dissolved in just the necessary quantity of sodium phosphate and a little $CaCl_2$; some investigators believe this condition prevails in milk itself.

The elemental analysis of casein derived from Cows' and from Human milk respectively are :—

Casein.

	Cows'.	*Human.*	
C	52·69 per cent.	52·24 per cent.	cf. Lane - Claypon "*Milk and its Hygenic Relations*" (1916), p. 37.
H	6·81 „	7·32 „	
N	15·65 „	14·97 „	
S	0·832 „	1·12 „	
P	0·877 „	0·68 „	

Casein is amphoteric in reaction, though its acidic functions are more pronounced, when it behaves as a tri-basic acid. When dissolved in dilute alkali a *l*-rotatory solution ensues.

Exactly as to how casein exists in milk is still a debatable point. Some authors believe it exists as a salt of lactic acid, casein-lactate. That lactic acid and casein do unite was shown by W. Van Dam (*Chem. Weekblad*, **7**, 1013 (1910)). This author, using Bredig's ethyl diazo-acetate method, determined the reduction of the H ions in solutions of lactic acid produced by adding various amounts of casein. The casein combined with a constant amount of lactic acid, viz., 4·25 per cent.

Revis and Payne infer a combination of casein with calcium phosphate. Richmond adduces evidence " that casein exists in milk as a calcium sodium salt, combined with one molecular proportion of tricalcium phosphate." (*Dairy Chemistry* (1914), p. 30.)

Casein is not coagulated when milk is boiled, but alterations occur in the molecule affecting the action thereon of digestive ferments, and in all probability increases the digestibility.

At higher temperatures than boiling, casein suffers partial coagulation, *e.g.*, at 130°–140° C., and Jensen and Plattner are of the opinion that the browning of milk so heated, is caused by the incipient breaking down of the casein." (*Rev. gen. du Lait* **IV**, 361–388 (1904–5).)

Cf. Also Conradi " Ueber den Einfluss erhöhter Temperaturen auf das Casein der Milch." *Münch. med. Wochensch.* **48**, 175 (1901).

The estimation of casein in milk is made as follows :—10 grs. of milk are diluted to 100 cc. and warmed to 42° C. 1·5 cc. of a 10 per cent. solution of acetic acid are added, and the mixture well stirred. The precipitated casein is allowed to settle for about 10 minutes, filtered on to a tared filter paper, dried at 105° C. and weighed. Ignite, and subtract the ash, plus the ash of the filter paper, from the total weight.

Casein is typically colloidal in nature as may be inferred from its behaviour in solution. It acts as a protective colloid, and stable sols of silver or cadmium sulphides are readily prepared by passing H_2S through solutions of silver or cadmium salts containing casein. Its gold number (determined in solution in ammonia) is 0·01, which stands quite high in the list of protective colloids arranged in the order of their gold no., *i.e.*, power of protection.

Casein combines with a fixed amount of NaOH (1 gr. requiring 0·88 millimol of NaOH) yielding a solution which has a normal electrical conductivity, but which does not pass through parchment when dialysed.

Chick and Martin showed that both acid and alkaline solutions of casein show an increase in viscosity as the amount of acid or alkali present is increased, indicating the greater adsorption of water by the casein-salt particles than by casein alone. (Cf. *Z. Chem. Ind. Koll.* **11**,102–105 (1912).)

Casein adsorbs acids, the amount adsorbed being almost directly proportional to the acid concentration. (Cf. TANGL, *Chem. Zeit.* (1908) **1**, 1288.)

The part played by casein in the colloid reactions of milk is very pronounced, and is discussed under "The Coagulation of Milk."

The Coagulation of Milk.

The coagulation or "curdling" of milk can be brought about by addition of acids, or by means of rennet, an enzyme obtained from the stomach of the calf. The casein in the milk is not acted upon by rennet in alkaline solutions, but only in acid or neutral solutions, and the greater the degree of acidity of the milk, the more rapidly does the rennet act. Dilution of the milk with water inhibits the action.

The natural curdling of milk is due to the acidity produced by bacterial action, which sets free lactic acid. Various investigators have proved that it is the actual hydrogen ion concentration that matters, and not the nature of the acid. The time required for clotting is proportional to the hydrogen ion concentration. (Cf. Michaelis and Mendlessohn, *Biochem. Zeit.* **58**, 315 (1915).)

These investigators found that the optimum concentration of hydrogen ions required for the precipitation of casein by acids in pure solutions or in milk = $2{\cdot}5 \times 10^{-5}$. The minimum concentration required was found by Allemann to be $1{\cdot}3 \times 10^{-5}$. (Cf. *Biochem. Zeit.* **45**, 346–358 (1912).)

Orla-Jensen showed that equivalent quantities of different acids are necessary to curdle equal quantities of the same milk at a given temperature, but the acids act at a different rate. (Cf. *Oversigt. K. Danike. Vidensk. Selsk. Forh.*, pp. 287–309 (1914).)

The whole question of the coagulation of milk by acids, and especially by rennet, is intimately connected with the question of the calcium content of milk, and any complete discussion must commence from this point.

In milk about 76 per cent. of the total calcium is combined with the casein; the total calcium content amounts to about 0·18 per cent. That calcium which is not united to the casein (about 24 per cent.) is present as phosphate and citrate. (Cf. Trunz, *Zeit. f. physiol. Chem.*, **40**, 263 (1903–4), Rona and Michaelis, *Biochem. Zeitsch.*, **21**, 114 (1909).)

When milk is heated, the calcium content falls. Thus Söldner showed that a milk containing 18 mgms. of Ca. per 100cc. when cold, lost 14 mgms. (*i.e.*, 17·5 per cent.) on boiling; in two other instances the loss amounted to 18 per cent. and 24 per cent. respectively. A similar decrease took place in the content of P_2O_5. Söldner inferred that the Ca. was united with phosphorus as mono- and di-calcium phosphate; this on boiling was converted into the insoluble tri-phosphate, and so precipitated. (Cf. Söldner, *Landw. Versuchs.* (1888), p. 351, Boekhout and de Vries, *Landw. Versuchs.* (1901), p. 221.)

Grosser, *Biochem. Zeit.*, **48**, 427 (1913) took a sample of milk and filtered it through a Bechold filter under a six atmospheres pressure of nitrogen, thus removing the colloidal constituents. The filtered milk was analysed raw, and also after being boiled for 15 minutes. The CaO content of the raw filtered milk was 23·4 per cent. of the initial (unfiltered) sample, and after 15 minutes boiling, only 18·0 per cent., or a loss due to heating of 5·4 per cent. of CaO. Repeating this experiment with butter-milk he found no change in the CaO content of the raw and the boiled filtrate, and inferred that the phosphorus and calcium had been spilt off from the casein owing to the acidity.

When milk is boiled the decrease in the calcium content is accompanied by a rise in the hydrogen ion concentration; see Milroy, *Biochem. Jour.*, **9**, 215 (1915). Approximately 8 per cent. of the total crude protein of fresh milk is not recovered by acid precipitation or heat coagulation. Cf. Palmer, *J. Ass. Off. Agric. Chemists*, **2**, part I., 144 (1916).

Rennet Coagulation.

When rennet is added to milk a separation into a precipitate (curd) and liquid (whey) takes place; the casein is transformed to a dyscaseose, "curd" being the insoluble calcium compound of this, and to a caseose (soluble). Rennet can clot 400,000 times its weight of casein in milk (Hammarsten), but it is a most remarkable thing that shaking the rennet renders it inactive. Cf. Schmidt-Nielsen, *Zeit. f. physiol. Chem.*, **60**, 426–62 (1909). An aqueous solution of rennet can be separated into fractions, having varying capacities for curdling milk by filtration through porous clay. See Korschun, *Zeit. f. physiol. Chem.*, **37**, 366-76 (1902).

Rennet acts best at 41° C., and the curd is then very firm; a fluffy, soft curd results at temperatures between 15° C. and 20° C. (at which temperature only 18 per cent. of the milk is curdled), and also at 50° C. (where 50 per cent. of the milk is curdled). The optimum range of temperature is from 36° to 45°.

Rennet is rendered inactive by prolonged storage, by shaking, by heating to temperatures over 60° C., and by addition of alkalies.

When milk is heated the action of the rennet is delayed, owing to the precipitation of calcium, but if $CaCl_2$ be added, the coagulation occurs in the normal way. Milk deficient in calcium salts requires a longer time for rennet-coagulation to take place. Cf. Söldner, *Landw. Versuchs.* (1888), p. 351; Ringer, *Journal of Physiology*, **11**, 464 (1890); Conradi, *Münch. med. Wochensch.*, **48**, 175 (1901); Kreidl and Lenk, *Biochem. Zeit.*, **36**, 357 (1911).

Interesting observations were made by Rupp, who observed that curdling by rennet was more rapid than with raw milk at temperatures between 55° C. and 65° C.; but slowed down at about 70° C. to nearly double the time; in this case, however, a finer grained coagulum resulted. Cf. *Bureau of Animal Ind. Bull.*, p. 166 (1913).

Although boiled milk is not curdled by rennet, a coagulation occurs on the addition of small amounts of $CaCl_2$. Lindet (*Comptes Rendus*, **157**, 381 (1913)), suggests that this is due to the interaction

of the $CaCl_2$ with the alkali phosphate and citrate in the milk, thus reducing the content of these, and rendering the casein less soluble.

During the action of rennet there is no change in the hydrogen ion concentration, but this is raised by addition of soluble calcium salts, and decreased by addition of ammonium oxalate. It is interesting in this connection to recall the fact that rennet acts best in acid solution, *i.e.*, in the presence of hydrogen ions. It was shown by Van Dam by the determination of electrical conductivity, that the coagulation time varied inversely as the hydrogen ion concentration, see *Zeit. physiol. Chem.*, **58**, 295 1908).

Mellanby has advanced an interesting theory for the rennet coagulation of milk, assuming it is due to the adsorption of the enzyme by the casein, and the subsequent precipitation of the enzyme-casein complex by the bivalent Ca ions of the milk. The quantity of ionised Ca salt required to effect precipitation is intimately related to the quantity of the enzyme adsorbed. Cf. *Jour. of Physiol.*, **45**, 345 (1912).

Bang observed that by adding rennet in fractions to milk, summation is noted, *e.g.*, the coagulation time on adding 0·1 cc. of rennet to 10 cc. milk is 8 minutes, and on adding 0·2 cc. four minutes. If, however, 0·1 cc. is added, and 4 minutes later another 0·1 cc., then clotting occurs two minutes after the second addition. No such summation occurs if the milk, after the first addition of rennet, is heated to 65° C.

Bang's many experiments led him to conclude that rennet is not a coagulating enzyme, since rennet of itself does not produce curdling, and the final act of curdling is not true coagulation, but is more akin to the precipitation of protein by neutral salts. Cf. Ivar Bang, *Skand. Archiv. Physiol.* (1911), **25**, 105–144.

Another conception of the rennet coagulation of milk is advanced by Schryver, *Proc. Roy. Soc.* (1913), **B. 86**, pp. 460–481. When solutions of calcium salts and sodium cholate are mixed, a clot results on heating. For salts which increase the surface tension of water, the greater their amount present, the shorter will be the time required for clotting to take place. Salts which decrease the surface tension decrease the time for coagulation, only up to a certain limit of concentration, above which the time is increased, or the coagulation entirely prevented. The inhibition of coagulation is attributed to the adsorption of simple molecules by the more complex colloids which are thereby prevented from coalescing. In milk the necessary materials exist, but the adsorption of simple molecules from the solution stops the coalescing. Schryver assumes that the enzyme clears the surface of the colloid from the absorbed substances thus permitting coalescence to occur. He asserts that in milk the clot formation depends on the presence of four series of substances present, viz., simple inhibitory substances, colloids, enzymes, and calcium salts.

Alexander advanced a somewhat similar notion, his view being that the casein is " protected " or held in stable suspension by the hydrophile colloid, lact-albumin, which rennet destroys, thus permitting the coalescence and precipitation of the casein particles. Cf. *8th Int. Cong. App. Chem.*, **6**, 12–14 (1912).

A very remarkable observation has been made by Kredil and Lenk (*Biochem. Zeit.*, **36**, 357 (1911)). They assert that sterile milk contained in sterile vessels will not clot when treated with sterile rennet. If, however, one dips into the mixture a non-sterilised body such as the finger or a glass rod, clotting sets in. A few drops of ordinary milk will also cause clotting.

In conclusion attention is directed to a most interesting paper by Bordas and Touplain on "Reactions of Curdled Milk due to the Colloidal State" (*Comptes Rendus*, **150**, 341 (1910)), where the view is advanced that the reactions of curdled milk hitherto attributed to the presence of enzymes may be explained by the colloidal state of the casein.

The Cellular Content of Milk.

Milk contains a large number of cells, falling into three main classes:—

(1) large uninucleated cells;
(2) multinucleated cells;
(3) small uninucleated cells.

These cells are formed either from the epithelium of the gland, or from blood and lymph. They may be estimated by centrifuging a given quantity of milk, *e.g.*, 10 cc. (preferably warmed to about 70° C.) and examining the sediment by a microscope. Very varied results are given, thus Russell and Hoffmann obtained figures varying between 4,000 and 1,000,000 cells per 1 cc. milk.

Cf. Hewlett, *Jour. of Hyg.*, **13**, 87 (1913); Howlett and Revis, *Lancet*, p. 855 (1915); Ross, *Jour. of Inf. Diseases*, **10**, 7 (1912); Russell and Hoffmann, *Jour. of Inf. Diseases*, **8**, Suppt. (3), 63 (1910).

Detailed knowledge of the nature of the cellular content of milk is still meagre, and the subject is only referred to here, as indicating another factor in the very complex colloidal nature of milk, since modern colloid chemistry is no longer the study of undialysable or glue-like substances, but of matter in a finely divided form, thus embracing grains, bubbles, capillary structures, animal cells, etc., and indeed any system of at least two phases, involving extensive surface areas.

The cell content of milk is mainly of interest to histologists who are investigating its relation to disease in the cow. *See* "*Public Health Dept.*, Washington. *Report No.* 78 (1912)."

Homogenised Milk.

Homogenised milk is the term given to milk which has been heated to 50–60° C., and then forced under great pressure through very small orifices, thus reducing the fat particles to very small diameters, *e.g.*, 1/100th of the original size. When such a milk is allowed to stand, practically no cream separation occurs at all, the milk remaining a homogeneous system.

This change in the dispersity of the fat leads to phenomena well known in colloid chemistry. The extension of surface area of the fat leads to greatly increased adsorption of the milk serum, and the

fat globules bear a " condensed layer " which is very tenaciously held. The rising of the fat globules is thus inhibited and no cream separates. Again, one cannot churn homogenised milk, since churning really implies the coalescing of the fat particles, and the separation of the milk serum.

The density of milk suffers no change on homogenising. The viscosity increases, due to casein adsorption by the fat globules, and the milk is thicker than ordinary milk of the same fat content. Wiegner reduced the average diameter of fat particles in milk by homogenising from $2{\cdot}9\mu$ to about $0{\cdot}27\mu$. From viscosity measurements he calculated that in ordinary milk about 2 per cent. of the casein is adsorbed, whilst the casein adsorbed by the fat in homogenised milk is about 25 per cent.

No change is produced in the molecular disperse constituents of the milk, as is indicated by the fact that the electrical conductivity, and the osmotic pressure (determined by F. Pt.) show no change.

If the homogenised milk is kept at a low temperature for some time the viscosity rises, and the fat particles do aggregate somewhat. Skim milk cannot be homogenised since it is nearly fat-free, and the casein present is already in a high degree of dispersity. Although mechanical means are of no avail, chemical means allow of this further dispersion of the casein, *e.g.*, when NaOH is added to skim milk, the viscosity increases rapidly with the concentration of the alkali.

Homogenised Cream.

When cream is forced through an homogenising machine at a pressure of from 3,000 to 4,000 lbs. per square inch, the fat particles become extremely small, and the product is very viscous. Separation of the fat again is rendered almost impossible, even on centrifuging; also it admits of neither churning nor whipping, and a colloid substance such as gum tragacanth must be added (*e.g.*, 0·1 per cent.) before a permanent foam can be produced. (Cf. *Koll. Zeit.*, **15**, 105–123 (1914).) Owing to its excessive thickness, homogenised cream is utilised in making ice-cream, since a cream containing about 17 per cent. of fat will, if homogenised, serve in an ice-cream as effectively as an ordinary cream of fat content 25 per cent., the final product having as good a body and texture, as well as " creaminess." An objection to homogenised cream is its peculiar " starchy " flavour, this being more apparent, the higher the temperature at which homogenisation is conducted.

The surface tension of homogenised milk is lower than that of the normal sample of milk.

Artificial Milk.

Of late years artificial milk has been prepared, and numerous patents taken out in this connection. It is simple enough to make a solution containing all the inorganic constituents of milk, but the organic (colloidal) constituents present a more difficult problem.

Certain nuts and beans contain proteid substances closely akin to gluten or casein in properties, *e.g.*, soya beans contain about 37 per cent. of such proteid matter, which can be brought into colloidal

solution by boiling with alkali, or salts which react alkaline, *e.g.*, sodium phosphate.

Thus, von Riegler [Fr. Pat. 461131 (1913)], prepared an artificial milk by dissolving gluten in caustic potash. It is usual, however, to emulsify a small quantity of oil (say 3 per cent.) with this colloidal solution of casein, and then to add small quantities of lactose, lactic acid, citric acid, etc., to render the similarity to milk more complete. Other ingredients which find their way into artificial milks are dextrin, malt extract, sucrose, dextrose, honey, NaCl, $NaH\,CO_3$, egg yolk, and preservatives.

Artificial milk can be "soured" by inoculation with lactic bacilli, and may be condensed, or made into artificial cream, butter, of cheese. Undoubtedly, a big future awaits this product, and it marks an especial advance in its use in margarine manufacture.

For further details cf. :—

Melhuish, Brit. Pat., 24572 (1913); Gossel, Fr. Pat., 451447 (1912), and Eng. Pat., 27860 (1912); Monahan & Pope, U.S. Pat., 1104376 (1914); Y.Y. Li, Eng. Pat. 30275 (1910); Kaufmann, Eng. Pat., 7296 (1913); Liebrich, Eng. Pat., 12355 (1898); Melhuish, Eng. Pat., 9626 (1915); Beckmann & Dyck, U.S. Pat., 1216052 (1917).

The Enzymes of Milk.

Enzymes are colloids, constituting a special class of catalysts, the catalysts being living organisms. Their presence in milk gives rise to some interesting facts explicable along the lines of our modern notions concerning colloid phenomena. The following enzymes are present in cows' milk:—

(*a*) Peroxidase.
(*b*) Reductase (indirect).
(*c*) Catalase.
(*d*) Amylase.

There is no conclusive evidence of the presence of proteolytic enzymes, lipolytic (fat-splitting) enzymes, or of lactase.

(a) *Peroxidase.*

This enzyme is always present in cows' milk, and its destruction by heat furnishes the basis of numerous tests devised to distinguish between pasteurised and unpasteurised milks. The first test used was to add tincture of guaiacum and H_2O_2 to milk, when, if per oxidase was present, a blue colour appeared. This test depended on the fact that guaiaconic acid (present in guaiacum) oxidises to a blue compound. It is noteworthy that H_2O_2 alone does not give this coloration with guaiaconic acid; an activator must be present to give the activating impulse to H_2O_2 and then oxidation can take place. Such an activator is peroxidase the enzyme of oxidation. The active system, peroxide plus peroxidase, is termed an "oxidase."

The enzyme is destroyed by heat; also it behaves catalytically, since extremely large amounts of peroxides can be acted upon, provided an oxidisable body be present.

The guaiacum test is replaced to a large extent by Storch's more reliable test involving the use of para-phenylene-diamine, and H_2O_2.

Cf. *Ber. des. Versuchst. d. K. Vet. u. Landb. Hochs.*, Kopenhagen; *Milchztg.*, **27**, 374 (1898).

A grey-blue coloration is given. It is necessary for this test, however, to use only 1 drop of H_2O_2 inasmuch as boiled cows' milk gives a blue coloration with p-phenylene-diamine and H_2O_2, if the latter is present in sufficient quantity. This is owing to the fact that the casein interacts with an oxidation product of the amine giving a blue compound. Such a milk would not respond to the guaiacol test, unless a peroxidase were added. Cf. Nicolas, *Bull. Soc. Chim.* **9**, 266–269 (1911–14).

The importance of the "peroxidase reaction" in the colloid chemistry of milk lies in the fact that most investigators now believe peroxidase to be a peculiarly active form of colloidal iron or manganese hydroxide, held in solution by a protective (hydrophile) colloid.

This protective colloid or emulsoid stabilises the system, and very likely confers specific properties such a coagulation by heat, acids, alcohol, etc. See Perrin, *J. de Chim. phys.*, **3**, 103 (1905); also, Röhmann and Shnamine, *Biochem. Zeits.*, **42**, 235–249 (1912).

Wolff, in his "*Contributions à la connaissance de divers phénomènes ozydasiques naturels et artificiels*" (1910), describes the full reproduction of all the actions of peroxidase with colloidal ferrocyanide of iron. Similarly, Sjolleman made an artificial oxidase with a colloidal solution of manganese hydroxide.

Lactic acid and hydrogen peroxide only interact very slowly; if now, a trace of ferrous sulphate be added, oxidation proceeds very rapidly indeed. A similar acceleration of oxidation can be brought about by addition of peroxidase. Thus the close similarity between the true inorganic colloid and the enzyme is shown clearly. In fact an artificial peroxidase of marked activity was described by Dony-Henault, *Bull. de la classe d. Sciences, Acad. roy. de Belgique*, pp. 105–163 (1908), viz., A solution of 10 grs. gum-arabic, 1 gr. manganese formate and 0·4 gram. sodium bicarbonate in 50 cc. water, is treated with alcohol. The ppt. is redissolved and reprecipitated by alcohol. The precipitate contains colloidal manganese hydroxide kept in stable solution by the "protecting" gum-arabic.

The "peroxidase reaction" is, no doubt, very closely connected with the iron content of milk, and it has been shown that there is quite sufficient iron in cows' milk to produce the reaction. The amount of iron in milk varies from 0·4 to 0·7 mg. per litre. Cf. Edelstein and von Csonka, *Biochem. Zt.*, **38**, 14–22 (1912).

Sarthou, *Jour. de Pharm.*, **2**, 583 (1910), and **3**, 49 (1911), showed that the peroxidase reaction can result when as small a quantity as ·0002 per cent. of iron is present.

The reaction is used in dairy laboratories to detect between raw and pasteurised milk, and although great differences of opinion are held as to the temperature at which the reaction is no longer given, it is generally agreed that milk pasteurised by heating to at least 70° C. for about 15 minutes, renders the peroxidase inactive. Cf. van Eck, *Zeit. f. Unters Nahr. u. Genussm.*, **22**, 393 (1911).

Other papers of much interest in the elucidation of the peroxidase reaction :—

Fenton, *Trans. Chem. Soc.*, **65**, 899–910 (1894).
Euler and Bolin, *Z. f. physiol. Chem.*, **57**, 80 98 (1908).
Herzog and Meier, *Z. f. physiol. Chem.*, **73**, 258–262 (1911).
Bach and Chodat, *Berichted. Chem. Ges.*, **37**, 1342–1348 (1904). *Arch. d. Sciences Phys. et Nat., Geneva*, **37**, 477.
Arnost, *Z. f. Unters. Nahr. u. Genussm.* (1905), **10**, 309.
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Sarthou, *Journ. de Pharm.*, **3**. 49 (1911).
Seligmann, *Z. f. Hyg.*, **50**. 97 (1905).
Utz, *Z. f. angew. Chem*, **16**, 871 (1903). *Oesterr. Chem Ztg.* (1904), p. 916.
Waentig, *Arb. a. d. kaiserl. Gesundh.*, **26**, 464 (1907).
Weber, *Milchztg.* (1902), pp. 657, 673.
Wirthle, *Chem. Ztg.* (1903), p. 432.

(b) *Reductase.*

It has long been known that if methylene blue be added to milk the blue colouration produced could often be destroyed by incubating the milk for a while, the time required varying with the samples of milk taken. The action is recognized as a bacterial one, and great efforts have been made to utilize it to measure the bacterial content of milk, but owing to the fact that only some, and not all, of the bacteria in milk are concerned in the reaction, the method was found very unreliable.

Schardinger (*Zeit. Unters. Nahrungs und Genussmittel* **5**, 1113–1121 (1902)) made some notable observations on the milk-reduction of methylene blue, establishing the following facts :—

(1) Fresh milk alone does not reduce methylene blue.
(2) Fresh milk to which an aldehyde (*e.g.* formaldehyde) has been added reduces methylene blue to the leuco or colourless base.
(3) This decolouration does not take place if the milk has been boiled.
(4) If bacterial development be permitted, there is no need to add aldehyde to milk to obtain the reduction of methylene blue.

The reaction in the absence of aldehyde is now termed the " direct reductase reaction," and in the presence of aldehyde, the " indirect reductase reaction."

Shardingr's M.B. reagent is obtained by diluting 5cc. of a saturated alcoholic solution of methylene blue with 195cc. of water. His F.M.B. reagent contains 5cc. saturated alc.; methylene blue + 5cc. of 40 per cent. formaldehyde + 190cc. water. In each case one uses 1cc of the reagent to 20cc. of milk warmed to 45° to 50° C.

The specific enzyme causing the reaction is termed " aldehyde-reductase " or " formaldehydase."

It is interesting to note that analogous reactions in inorganic chemistry are obtained, using the colloidal solutions of metals of the platinum group. Thus aqueous solutions of hypophosphites are oxidised on the addition of fine-divided palladium :—

$$H_3PO_2 + 2H_2O \; H_3PO_3 + H_2 + H_2O.$$

Formaldehyde is unaffected by colloidal palladium, but in the presence of methylene blue, nitrates, indigo, or other easily reducible bodies, the aldehyde is oxidised, and the reducible bodies act as "receivers" for the hydrogen.

Bach, *Arch. Sci. phys., Génève*, **32**, 27–41 (1911), assumes the existence of a perhydride of oxygen in the water, H_4O_2, analogous to peroxides in the peroxidase reaction. Such a compound has never been isolated, and one feels that its assumption is not required, since the theory of the activation of the water by the enzyme amply meets the case.

An enormous mass of work has been done on the Schardinger reaction, but a recent paper by Lee and Mellon (*J. Ind. Eng. Chem.* **9** 360 (1917)), ably summarises the present position. The conclusions reached are:—

(A) Methylene blue as it occurs in Schardinger's reagent F.M.B. is not decolourised by:—

(i) Normal fresh milk in less than 20 minutes. When decolouration was effected in 10 mins. or less, the milk was found to contain 1,000,000 or more micro-organisms per 1 cc.

(ii) Milk pasteurised at 70° C. for 10 mins., unless approx. 48 hours have elapsed since the milk was pasteurised, or until the bacteria have had time to multiply sufficiently.

(iii) Old milk in which formaldehyde had inhibited the growth of bacteria.

(B) Schardinger's reagent, F.M.B., is as a rule decolourised by normal milk allowed to "age" under ordinary conditions of temperature for 24 to 48 hours.

(C) Pasteurisation increases the time required for the decolourisation of the reagent.

(D) In general, no proportionality exists between the time required for the decolourisation of the reagent and the number of bacteria in milk. In a given sample, however, a general relation seems to exist between the two up to a given point of acidity.

(E) Inasmuch as there is no absolute parallelism between the *number* of bacteria in the milk and the *time* required to decolourise the reagent, but that the relationship seems to exist in a given sample of milk, it would indicate that reductase is of bacterial action, but that not all bacteria found in milk produce this enzyme.

(F) It seems probable that formaldehyde either gradually retards the action of the reductase or destroys it.

Several very interesting observations on the Schardinger reaction have been made by various investigators. Thus:—

Utz (*Zeit. f. angew. Chemie* (**16**), 871 (1903)) showed that sour milk could be made to give the reaction by adding to it NaOH or other alkalies.

Rullmann (*Biochem. Zeit.* (**32**), 446 (1911)) showed that instead of HCOH one could use formic acid for the F.M.B. test.

Römer and Sames (*Zeit. f. Unters. Nahr-u. Genussm.*, (**20**), 1 (1910)) showed that milk which failed to respond to the Schardinger test would do so if a small quantity (less than 1 per cent.) of ferrous sulphate were added. The ferrous sulphate solution must not be boiled.

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Shroeter, *Centralb. f. Bakt.* ii. **32**, 181 (1911).
Siegfeld, *Zeit. f. angew. Chem.* **16**, 764 (1903).
Smidt, *Arch. f. Hyg.* **58**, 313 (1908).
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(*c*) *Catalase.*

This very remarkable enzyme is universally present in cow's milk. It acts on hydrogen peroxide to produce *molecular* oxygen, this result being very unique, since one usually obtains 'active' or atomic oxygen when H_2O_2 is decomposed. The generally-accepted explanation is that the enzyme attacks two molecules of H_2O_2 simultaneously, thus:—

$$2HOOH = 2H_2O + O_2$$

Catalase in milk is estimated by measuring the volume of oxygen liberated when a given quantity of H_2O_2 is added to a given quantity of milk. Usually one takes 20cc. of milk and 5cc. of a 3 per cent. H_2O_2 solution, using a special apparatus, which is kept in the water-bath during the course of the test.

The catalase is most probably of bacterial action, and its amount increases when the milk grows stale. Cream contains a larger percentage of catalase than the rest of the milk. So far no figure for the normal catalase content of milk is agreed upon, though such a standard is desirable as an indication of the bacterial content of a given sample.

Oxidising agents such as chlorates, nitrates, and hydrogen peroxide, and poisonous bodies like HCN or mercuric chloride are especially harmful to catalase; indeed, Euler has shown that a strength of 1 in 1,000,000 HCN reduces the reaction velocity of catalase by one half.

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For a detailed study of the enzymes of milk cf Lane-Claypon, Reports to the Local Government Board on Public Health and Medical Subjects ' (New Series), No. **76** (1913).

(*d*) *Amylase.*

This enzyme is only present in small amount, *e.g.* Lane-Claypon found that 10cc. of cow's milk at 37° C. hydrolysed about ·001 to ·002 grm. of starch in three hours. The starch is converted to dextrins.

Koning found the amylase activity of milk to be destroyed on heating to 68° C. for 45 minutes.

Margarine.

Margarine technology presents many questions of great interest to the Colloid Chemist, and offers a wide field of research in pure physical chemistry.

Margarine is a substitute for Butter, certain animal and vegetable oils and fats replacing the familiar butter fat. Thus stearine, oleo lard, cocoanut oil, kernel oil, cottonseed oil, and arachis, kapok, maize, and wheat oils are all in present use. The oils and fats are liquefied together in certain proportions, depending on the quality of the margarine required, and then churned with soured milk to form an emulsion. This emulsion is rapidly cooled, either by means of a spray of iced water under pressure, or by flowing on to well-cooled revolving drums. The product in each case is then worked up in drums or rollers to the required buttery texture and consistency.

For an account of modern Margarine Technology, cf. Clayton, J.S.C.I., **36**, 1205–1209 (1917).

In the manufacture of margarine, the process of emulsification is of first importance. " The object of churning is to imitate the emulsion found in cream and milk, where the fat globules have diameters ranging from 0·01 mm. to 0·0016 mm. and remain as discrete particles. The general theory of emulsification indicates that with two immiscible or only partly miscible liquids, two types of emulsion are possible, each constituent being in turn the disperse and then the continuous phase. For concentrated solutions a third (emulsifying) agent is required. Where oil is to be the internal or disperse phase, the emulsifying agent should be capable of lowering the surface tension of the external or continuous medium, and should be viscous, as is glycerin, or an emulsoid, like gelatin. If oil be dispersed in water, a stable emulsion can be made, the stability depending on the minuteness of the oil drops, this in turn being a result of the efficiency of the emulsifying apparatus. If, however,

water be dispersed in oil, a very unstable system is produced, separation into two layers taking place as soon as beating-up ceases. Now milk by virtue of its colloidal content is an excellent emulsifying agent, when oil is the disperse phase. Consequently if milk be in a churn in bulk, and oil is slowly fed in, with continuous agitation, an excellent emulsion of great oil concentration can be produced, and will set to a homogeneous mass afterwards. But if the oil be in the churns in bulk, and milk is fed in, a very unstable system results, which easily separates into layers on stopping the agitation for a while. This has been proved many times and the explanation seems clear:—To get a suitable emulsion of water in oil, one would require an emulsifying agent which should form an *oil*-soluble colloidal solution but in milk the colloids are *water*-soluble. Both theory and practice condemn any form of churning which would lead to emulsion with oil as the continuous medium. Such emulsions when cooled by iced water, or on drums, solidify with clot formation, and the resultant margarines are 'spotted' in texture." (Clayton, *Loc. cit.*).

In order to aid emulsification many colloidal substances have been proposed for use in making margarine, *e.g.*, starch, gelatin, glycerin, egg-yolk, lecithin compositions, etc. These agents are added to the milk, and certainly do have a most helpful effect when churning. So small a quantity as 0·1 per cent. of glycerine added to the milk or oils (since it mixes with oils) leads to much improved emulsification. The usually-accepted theory accounting for this phenomenon is that the emulsifying agent forms a membrane or film around the oil globules and so prevents their coalescence.

Egg-yolk, usually compounded in Sesame Oil, has been fairly widely used in margarine works as an aid to churning, and it is very interesting to note that egg-yolk, containing about 10 per cent. of lecithin, and 15 per cent. albumen, both colloids, is an exceptionally stable emulsion, not separating into phases even on long standing or centrifuging.

Practically all the physico-chemical questions relating to margarine involve discussion of emulsions, and unfortunately rather too little is understood concerning them, whilst the physical chemistry of a *solid emulsion*, such as margarine as a finished article presents, is only in its infancy.

The first question which arises is concerned with the determination of the nature of the external, and disperse phases of a given sample of margarine, *i.e.*, is it a solidified oil-water or water-in-oil emulsion? That is a hard question to answer. With liquid emulsions the problem is easier, and three methods at least may be employed to differentiate:—

(1) By a *Kataphoresis test*, since the internal phase being negatively charged will wander to the anode.

(2) *Indicator Method.* This method depends on the fact that if one adds an oil-soluble dye to an emulsion, the dye will spread if the oil be the continuous medium. Thus Robertson used Sudan III, a red dye, in his work on emulsions of olive oil in water (*cf. Koll. Zeit.*, **7**, 7–10 (1910)). With an emulsion of oil in water, the colour

would not spread, but be confined to those globules of oil with which the colour rains were actually in contact.

(3) *Drop Method.* The principle involved is that one can dilute an emulsion by adding more of the continuous medium. (*See* Newman, *Journ. Phys. Chem.*, **18**, 34–55 (1914).)

Now these methods are not suitable for a solid emulsion such as margarine, though the staining with dyes, followed by an examination of a thin film under the microscope, sometimes gives valuable indications. The electrical conductance of margarine, the heat conductance, and the viscosity would seem to offer suitable lines of research in this problem of distinguishing the nature of the phases.

If the margarine were an oil-in-water emulsion, one would anticipate a possible electrical conductance (since there is at least 1 per cent. NaCl present), on the same lines as the conductivity through a set jelly, *e.g.*, gelatine. But with a water-in-oil emulsion, the conductivity (if any) would be very small indeed, inasmuch as the contiguous particles are now fat, which is characterized by its insulating properties.

Again, it would be most interesting to investigate the heat conductivity of two solid emulsions having inverted phases. The corresponding case of the heat conductivity of a set jelly still remains for research.

Possibly information would be afforded by the viscosity of a solid emulsion. The rôle of viscosity in colloid researches is increasingly manifested, and " the great importance of viscosity measurements as the most delicate means of tracing slight changes in colloidal solutions is fully recognized " (E. Hatschek). Indeed, with an emulsion like margarine, with an average ratio of oil to water, 3·6 : 1, one would anticipate notable variations in viscosity depending on whether the oils and fats constituted the disperse or continuous medium.

There are many other problems of a colloid nature connected with margarine, but they are only apparent to one actually in contact with the entire process. Thus, why does soured milk yield a better emulsion with the oils and fats than sweet milk? Certainly, no very sound theory is as yet proposed, though it is interesting to note that oils and fats containing a small percentage of free fatty acids will much more easily emulsify with water than will neutral oils or fats. Since sour milk is distinctly acid (lactic acid), there would seem to be some connection here, but mineral acids cause emulsions to " break."

Finally, in connection with margarine manufacture, one research of great importance is suggested by the use of the various emulsifying agents previously referred to. So far, little work has been published describing what one may term the ' emulsifying efficiency ' of such an agent. Thus, to make a concentrated stable emulsion of an oil in water, one adds gelatine, starch, gum, flour, etc. It would be very interesting to arrange these substances in the order of their capacity or power of stabilising a standard-strength emulsion, and then investigating the possible connection between the " emulsifying efficiency " and the gold number, viscosity, surface tension, etc., of their pure solutions in water (cf. Moore & Krombholz, *Brit. Journ. Physiol.* **22**, 54 (1908)).

Cheese.

Cheese is obtained by the rennet curdling of milk. The curd is cut up small and the whey expressed from it; the mass is then salted and allowed to ripen by bacterial and enzymic action. There are many kinds of cheese, but for the purpose of this paper their description is unnecessary. Very little indeed is known of the colloid chemistry of cheese, except that portion relating to the action of rennet on milk and the subsequent production of curd.

The following are some typical analyses of hard cheeses:—

	H_2O.	Fat.	Protein.	Ash.
	Per cent.	Per cent.	Per cent.	Per cent.
(*a*) Stilton...	20·30	44·00	23·70	2·75
(*b*) Cheshire	34·70	33 30	26·10	4·30
(*c*) Cheddar	33·90	29·05	27·37	4·05

The structure of cheese varies from a dough-like to a granular texture, and it is in this conection that the only colloid researches have been made on cheese.

Van Dam investigated the swelling of casein under the influence of common salt and lactic acid. He ascertained the solubility of casein in solutions of NaCl (5, 3, and 1 per cent.) containing lactic acid, and obtained curves showing the relation between the dissolved casein and the concentration of the hydrogen ions. Cf. van Dam, *Gedenkboek. aan J. M. van Bemmeln* (1910), pp. 102–107.

Chick and Martin published results on the viscosity of casein sols, which bear somewhat on this problem. In the case of both alkaline and acid casein solutions, the viscosity increases with the quantity of alkali or acid present, which indicates that the casein-salt particles have a greater adsorptive power for water than has casein itself. Cf. *Z. Chem. Ind. Koll.* **11**, 102–105 (1912).

The most important contribution to the subject, however, has been made by Allemann and Schmid (*Landw. Jahrb. Schweiz.* **30**, 357–383 (1916)). They investigated ' the elasticity of the coagulum produced in milk by rennet.'

An apparatus was employed which measured the resistance which the curd offered to a vertical rod carrying three concentric rings. Thus they were able to investigate the effect of time, concentration of rennet, concentration of acid, and other factors, on the curd produced. It was found that the elasticity of the curd increased in direct proportion to (*a*) acidity of milk, (*b*) concentration of the rennet, (*c*) addition of soluble calcium salts, (*d*) rise in temperature. No apparent maximum of elasticity was ascertained with ascending temperatures, though the time required for coagulation reached a maximum at 41° C. Agitation during curdling inhibits the velocity about 8 per cent. With cold milk, a longer time was required for curdling, and the resulting curd had a decreased elasticity.

The whole question of the structure of cheese still remains open for research, as also does the question as to the physical state of the fat globules present. *See* Stocking, '*Manual of Milk Products*,' chap. 9 (1917).

Ice-Cream.

Ice-cream manufacture provides an interesting case of the practical value of the so-called ' protective action ' of colloids.

Alexander (*J.S.C.I.* **28**, 284 (1909)) writes:—' It is a well-known fact to practical ice-cream makers and amply proven by experience, that ice-cream made without eggs, gelatin, or some similar colloidal ingredient, is gritty, grainy, or sandy, or else soon becomes so on standing, whereas ice-cream made with small quantities of colloids possesses that rich, mellow, velvety texture, so much in demand.' (Cf. also Alexander (*Zt. Chem. Ind. Koll.*, Feb., 1909).)

Now ice-cream contains casein, and the action of the added (hydrophile) colloid is to ' protect ' it from coagulating. Gelatin is especially advantageous, and as little as 0·5 per cent. suffices to render the ice-cream smooth in texture. Incidentally, the digestibility is increased too by addition of gelatin. (Cf. discussion on the digestion of milk curd in the stomach.) Besides the protection of the casein, it is most interesting to note that the small ice crystals are also ' protected ' by the colloidal binders added. An ice-cream having been whipped during freezing, contains numerous small ice crystals, which on standing coalesce to form coarse grains. This coalescence is decidedly inhibited by gelatin, gum tragacanth, and starches, thus retaining the smooth texture so desirable in a first grade product. (Cf. Stocking ' *Manual of Milk Products*,' Chap. 14, (1917).)

An interesting paper on ' The Effects of Binders upon the Melting and Hardness of the Ice-Cream,' was published by Holdaway and Reynolds (*Virginia Expt. Stat. Bull.* **211**, 3, (1916)). It is here shown that as the per cent. of fat in plain ice-cream increases, the cream becomes softer, and if too much fat is present a soft fluffy product results owing to ' whipping.' Ice-cream made from 8 per cent. cream was no harder than from 19 per cent. cream, while 30 per cent. plain cream was much softer than either. The fat, however, rises to the melting point.

Now, if gelatin be added a harder ice-cream results, with a higher melting point. The hardest and most heat-resisting cream is given by a medium per cent. of fat and a large amount of gelatin. Gum tragacanth (also a protective agent) may be used, in which case the ice-cream produced is harder than usual (plain) but softer than when gelatin is used. One would expect this result, since the protective powers of the two colloids are very different, as will be seen by a comparison of their gold-numbers, viz.:—

Gelatin	0·005 to 0·01.
Gum tragacanth	about 2·0.

If too much gum tragacanth is used, a very slimy cream results; in any case it is far inferior to gelatin ice-cream of any composition.

Some manufacturers use starch as the agent to ' smooth ' their ice-cream, but although a better product than normal (plain) cream results, the texture is much more grainy than the ice-creams containing gelatin or gum. One expects this to be the case, since starch is only a poor protecting colloid, the gold value of wheat starch being about 5, and of potato starch about 25.

Eggs are, of course, good binders, since egg-albumen (with a gold value of 0·15 to 0·25) is a strongly-protecting colloid.

In the literature concerning ice-cream one finds the term ' filler ' applied to these added colloids, but the term ' binder ' is probably to be preferred.

This problem once again opens up the question as to the ultimate action of a protecting colloid; the usually accepted idea is that the colloid forms a membrane around the particles of the suspension material and so prevents the coalescence. This is Bechold's adsorption view. (Cf. *Zeit. phys. Chem.* **48**, 385 (1904)).

[The question of ' protection ' is considered in detail in W. D Bancroft's report upon Peptization and Precipitation. Cf. p. 2. W. C. M'C.L.]

COLLOID CHEMISTRY IN PHYSIOLOGY.

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Introductory.

Since all physiological processes occur in complex heterogeneous systems, both coarsely heterogeneous and colloidal, it is clear that a complete discussion of the subject would include practically the whole of the science. Even in the functions of the central nervous system, which might seem most distant from colloidal chemistry, we have to take account of the properties of the membranes which intervene between the component elements, and certain observations made on these elements themselves will be referred to incidentally in the following pages. There are, however, some regions in which colloidal properties play a more obvious and better known part. These concern especially the nature and properties of protoplasm itself, including the membrane which surrounds it, and the relationship of their constituents to electrolytes. Another problem that will appropriately be considered is the nature and functions of enzymes, which regulate the chemical reactions of the living organism. And finally, the remarkable properties of haemoglobin in relation to the transport of gases require brief consideration.

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I. Protoplasm and Cell Contents.

When a simple unicellular organism, such as amoeba, which consists of so-called " naked " protoplasm, is examined under the microscope, it is seen to contain a variety of granules and other inclusions of comparatively large size. These lie in a clear, apparently structureless, substance which is in contact with the water in which the animal lives. For this latter reason, the protoplasm is said to be naked, in contradistinction to vegetable cells, such as algae, which are clothed with a cellulose coat.

Since the amoeba and the water are two distinct phases, which do not mix, there is a surface tension at the interface of contact. Owing to the curvature of the surface being concave towards the animal, this surface tension results in a pressure exerted on the contents. Now the tension can be lessened by the addition of various substances to the water and, when this takes place locally, a protrusion is brought about by the internal pressure due to the higher tension of other parts of the surface. Under the ordinary microscope, these protruded portions, "pseudopodia," appear to be clear and structureless like water. This fact can be seen in the drawings made by various observers. But when they are examined by the brilliant lateral illumination of ultra-microscopic methods, light is diffracted by minute particles which are present in great number. These become visible as bright shining dots against the dark background. The general effect, when the illumination is at its best, is that of a multitude of brilliant points in rapid, shimmering motion, occasionally more distinctly vibratory. This is the phenomenon first seen by the botanist Robert Brown, in 1828, and hence called "Brownian movement." Its nature has been cleared up by Perrin, in a masterly series of researches, now well known. It was shown to be due to irregular bombardment by molecules of the liquid in which the particles are immersed and only present when the mass of a particle is small enough to enable the difference between the resultants of the unequal bombardment on opposite sides to be great enough to move it. The chief observations on Brownian movement in protoplasm are due to Gaidukov (1910) and to Price (1914).

The observation shows at once that protoplasm in its simplest form is a liquid, because otherwise particles present in it would not be free to move. The existence of these particles in the liquid shows that we have a colloidal solution of the kind called by Graham a hydrosol, which consists of a suspension of minute particles of a solid in water, or of an immiscible liquid in water. In other words, protoplasm is a dispersion of a more solid phase in a more liquid or watery phase.

It is necessary to emphasise this fact, because earlier observations, made on cells which had been coagulated by the action of heat or of precipitating reagents, were believed to show the presence of a continuous network. Although it is possible that a network might be produced under such conditions, it is to be remembered that, owing to the similarity in refractive index and in colour of the two phases, it is impossible to examine such preparations under conditions of illumination adequate to eliminate diffraction images, which readily take the form of networks when a regular series of dots is examined. The work of Hardy (1899) and of Alfred Fischer (1899) has shown, moreover, that a great variety of structures can be produced by the action of fixing reagents on cell protoplasm. It is impossible to say which of these corresponds to the living state. Most probably none do so, since we know that living protoplasm is a liquid.

There is further evidence that this is the correct statement. When the cell of an alga is taken in as food, water is either taken with it or is excreted around it. Whatever may be the shape of the

particle itself, the shape of the liquid drop in which it floats is always spherical. In other words, it takes the form conditioned by the free play of its surface tension. This would not be possible unless it were free from the constraint exerted by solid structures. A similar conclusion may be drawn from the shape assumed by a mass of protoplasm when stimulated in any way; this is also spherical. Arthur Lister (1888), again, found that *Badhamia*, an organism which, at one stage of its existence, takes the form of masses of flowing protoplasm, filled with the brown spores of a fungus on which it feeds, can be filtered clear through wet cotton wool. It seems impossible that anything but a liquid could be separated up into the fine threads necessary to pass through the cotton wool and reunite again into its original form. Chambers (1917) has introduced some beautiful methods of micro-dissection. He finds that the needle can be repeatedly drawn through protoplasm without injuring it in any way. Very little resistance due to viscosity is experienced, as shown by the fact that it is only the granules in immediate contact with the needle that are displaced. There is no trace left behind in the track of the needle.

It is remarkable that the only consistent cells of the tissues of higher animal organisms that have been examined in the living state by ultra-microscopic methods are those of the central nervous system. This has been done by Mott (1912) and by Marinesco (1912), independently. They agree in the statement that the protoplasm of these cells shows numerous particles in Brownian movement and is therefore a liquid. There is no sign of the large masses (' Nissl granules ') nor of the ' neuro-fibrils ' seen in fixed and hardened preparations. According to Mott, the " granules " themselves consist of a hydrosol, surrounded by an envelope which stains deeply with methylene-blue. Marinesco was able to see local reversible changes taking place spontaneously. Areas of more brilliant, that is, larger, particles appeared now at one part, now at another of the cell.

While the state in which protoplasm usually is seen is that of a hydrosol, certain observations made by Kühne (1864), by Gaidukov (1910), and by Price (1914) indicate that it may take on, temporarily, the state of a gell. In this state the Brownian movements are arrested, because the particles become fixed in position. It is evidently related to functional activity. I have myself been able to produce it by weak electrical stimulation. What one sees is a sudden cessation of the shimmering movement, as if frozen solid. The condition is very transitory and requires careful adjustment of the illumination to show it. Price (1914) describes the protoplasm of a resting spore as being in the gel state, changing to the hydrosol on germination. When a cell dies it passes to the hydrogel condition. It is of some interest to note that the protruded pseudopodium of an amoeba remains in the hydrosol state, a fact which suggests that it is producel by external influence rather than by a " vital " reaction on the part of the animal.

What do we know of the mechanism by which such changes might be produced? There are two researches in particular which throw light on the question—that of Hardy (1900) on gelatin and

that of Clowes (1916) on emulsions of oil and water. Hardy examined under the microscope the phenomena which occur when a warm gelatin sol sets to a gel on cooling; the first sign of change is that the ultra-microscopic droplets of the dispersed phase unite to form larger drops. If the solution is moderately concentrated, these drops unite together to form a network, but the watery phase is still continuous. On the other hand, if we begin with a solution of high concentration, the drops which first separate can be seen by their refraction to consist of the watery phase, so that the phase relations are reversed when compared with the former kind of gel. Thus the network may consist either of the more solid or of the more liquid phase. The properties vary accordingly. If the liquid phase is the continuous one, it can be pressed out by squeezing. If the more solid constituent is the continuous phase, liquid cannot be pressed out except by a pressure sufficient to filter it through the more solid phase.

The work of Clowes took its departure from an observation of Bancroft (1913) that a mixture of oil and water can be made into a permanent emulsion in two ways. One of these consists of drops of oil suspended in a continuous watery phase, as in cream; the other is of drops of water suspended in a continuous phase of oil, a in butter. The former system is produced when sodium soaps are used as emulsifying agents; the latter if calcium soaps are used. Clowes (1916) showed that an emulsion of the former kind could be converted into one of the latter by shaking with a solution of calcium chloride, while the latter could be changed into the former by shaking with sodium hydroxide. The changes may perhaps be realised by the illustration of a set of islands joining together so as to be transformed into a series of lakes surrounded by land. Clowes describes further experiments which will be more appropriately discussed in the section dealing with the cell membrane. He shows how the nature of the system depends on the relative surface tension at the two sides of the soap film which is formed by adsorption at the boundary surface between the two phases. It will be obvious that the physiological properties of the two kinds of system, the liquid and the gel, with the possibility of converting one into the other by phase reversal, must play an important part in cell life.

That there are possibilities of the formation of membranes, doubtless of a gel nature, within the protoplasm of a cell is shown by the fact that different reactions can take place at the same time in different parts of the cell, notwithstanding the general liquid nature of its contents. The view that the organization of the cell is of the nature of many minute factories, in which various operations are being carried on under the influence of the structure of the cell, is at the present time rapidly displacing that of " giant " molecules with " side-chains," which were supposed to be continually split off and exchanged for other chemical groups. The question is discussed in the British Association address of Prof. Hopkins (1913). Put in another way, limitation of the point of view to that of pure structural organic chemistry is showing itself to be incapable of explaining physiological reactions. Protoplasm is an extraordinarily complex heterogeneous system of numerous phases and components,

continually changing their relations under the influence of electrolytes and other agents.

It has frequently been felt to be a difficulty, from the standpoint of energetics, that cells use energy for purposes in which it is not easy to make out what has become of it. Warburg (1914) suggests that it may be required for the keeping apart of substances which would mix by diffusion, for the preservation of semi-permeable membranes, the restriction of osmotic interchange and so on, all of these phenomena being manifested in microscopic or even ultra-microscopic dimensions. A discussion of phase relations in protoplasm in connection with equilibrium and energy will be found in the essay by Zwaardemaker (1906).

A property of emulsoid colloids which has its importance in the present connection is their capacity of taking water by what is often called "imbibition." The distribution of water between the two phases can be varied to a large extent by the presence of electrolytes and other agents. Whether imbibition is mainly or entirely an adsorption of water at the *surface* of the constituent elements, as is indicated by the experiments of Posnyak (1912) and by some which I did myself on gelatin ("General Physiology," p. 101), it is clear that the concentration of solutes in the liquid phase must be raised thereby. Since the position of equilibrium in reversible hydrolytic reactions, catalyzed by enzymes, depends on the concentration of water present, we see how at one time a synthetic product, such as glycogen, is hydrolyzed, and at another time glucose is synthesized to glycogen by the same enzyme. What is required is merely a means of varying the free water, and the possibility of this is provided by the presence of highly dispersed emulsoid colloids.

In addition to the highly dispersed systems discussed above, protoplasm usually contains various larger aggregates and structures. Chambers (1917) calls the small particles visible under the ordinary microscope, "microsomes," and the larger ones, "macrasomes." He shows that the former are stable, the latter very sensitive to injury. There are also certain granules, of various forms, called 'mitochondria.' Cowdry (1916) has devoted special attention to these and finds that they are stained in the living state by dyes which contain a diethyl-safranin group, such as Janus-green B, and are apparently composed of albumin and lecithin. In the living state they are continually changing shape, and especially in cells during activity.

In the present state of knowledge, it would be unprofitable to speculate further on the functions of these different inclusions. The same may be said of the *nucleus* of the cell. That this is essential to continued life, growth, and subdivision is clear. Much attention has been given to the series of changes which it undergoes in the last process, called "mitosis," or karyokinesis." They are obviously due to the orderel arrangement of certain vectorial forces, having a definite focus of origin, but we are still in the dark as to their meaning. Much importance has been attached to the number of distinct staining elements, "chromosomes," produced at a particular stage of the process.

Unwarranted conclusions are sometimes drawn as to the chemical nature of substances found in cells from their behaviour to dyes. The theory of dyeing has been described in an earlier report by King (1917) to which the reader may be referred. There are many factors which play a part in addition to chemical composition. Fischer (1899) has shown that the same substance stains differently according to the size of the particles in which it is found. The sign of the electric charge is also of importance. The meaning of the fact is still obscure. Nervous substance has a special "affinity" for methylene-blue and other thiazine dyes, but also for some safraninazo dyes, which have no chemical relationship to the former.

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II. The Nature and Permeability of the Cell Membrane.

Although protoplasm is a hydrosol of low viscosity, it does not mix with water, remaining, while alive, as a separate phase. If "killed," as by an electrical shock or the application of an anæsthetic, it freely mixes with the surrounding watery solution. In the

normal state, it must be surrounded by a film or membrane of some kind, which prevents escape of the cell contents. We may draw a similar conclusion from the fact that the products arising from digestion of the food particles in protozoa, although consisting of such freely diffusible substances as glucose and amino-acids, are not washed out. Much discussion has arisen as to the nature and even the existence of such a membrane. In the present Report, space will not permit of discussion of all the work which has been devoted to the problem. Attention must be directed to those aspects of it which appear to the writer to be of essential importance and to the conclusions to be drawn therefrom. These conclusions will sometimes differ from those of the investigators themselves and the reader may not always be inclined to agree with the interpretations given in this place.

It has been pointed out (Bayliss, " General Physiology," p. 128) that, according to the Principle of Willard Gibbs, which is a consequence of the tendency of free energy to decrease, as stated by the second law of energetics, if there are in the cell contents any substances which lower surface tension, these must be concentrated at the interface between the protoplasm and the surrounding liquid. Moreover, Ramsden (1904) has shown that, in many cases, as solutions of bile salts, quinine or saponin, this concentration at the surface may be so great as to exceed the solubility of the substance in question, which is then deposited in a solid form, producing a film of more or less rigidity. In addition to this, Chambers (1917) finds that the extreme outer layer of the protoplasm has the properties of a gel. The change from sol to gel has been discussed in the preceding section. In the present case, it is doubtless due to the molecular forces at the surface. It should be noted that this outer layer of the protoplasm is not identical with the membrane to which the cell owes its semi-permeable properties. When a dye is unable to enter a cell, it does not stain this " hyaloplasm " stratum, so that the membrane which stops it has a more external situation. We see that there is every reason to expect the presence of a film on the surface of cells and that it would be reversible, existing only on the boundary surface and formed anew whenever any fresh surface is produced. These considerations also give us a clue as to the chemical composition to be looked for. In addition to the components of the hydrogel, whatever they may be, but almost certainly protein of some kind, we shall expect to find more especially those constituents of the cell which lower the surface tension of water to a marked degree; in other words, all compounds of a fatty nature, and of these lecithin is known to be universally present.

If we add certain dyes, such as aniline-blue or congo-red, to the water in contact with the protoplasm of a cell, we notice that it does not enter; the cell remains unstained. That this is not due to an obstruction anywhere but on the surface is shown by the fact observed by Kite (1913) that, if introduced by a capillary tube into the interior of a cell, congo-red freely and rapidly diffuses throughout the contents. Now it was observed by Nägeli (1855), and confirmed by Pfeffer (1890) and others, that if a mass of protoplasm be broken

up into several smaller pieces, these parts when free assume a spherical shape, and form at once on their surfaces a layer with the same properties as regards permeability as the original protoplasmic membrane had.

If the cell substance is in contact with a liquid containing various substances in solution, as in the tissues of the higher plants and animals and in the case of the vacuoles in the interior of the cell, then the surface film will contain constituents of both phases and its properties will not be identical with those of a membrane formed in contact with water only. Evidence of this was found by Osterhout (1913).

It is obvious that the properties of the cell membrane as regards permeability to solutes both in the external liquid and in the interior of the protoplasm must play an important part in the life of the cell. While it is impossible to deny that a film of some sort must be formed, it is held by some investigators that sufficient evidence does not exist that it is possessed of the property of semi-permeability, at all events as regards crystalloids (see especially Moore and Roaf, 1908). If this be so, it is clear that the escape of such constituents from the cell must be prevented by their existence therein in fixed combination with solid parts. The evidence on this question must be examined.

There is no doubt that the salts present inside a cell may differ, not only in concentration, but in their chemical nature, from those in the external liquid. Perhaps the most striking case is that of the red blood corpuscles of the rabbit. Abderhalden (1898, p. 100) found that the blood serum contains 0·44 per cent. of sodium salts, while the corpuscles contain none at all; whereas the corpuscles contain twenty times as much potassium salts as the serum does. Similar facts have been described in the case of the muscle cells. The behaviour towards acid and alkali is interesting. Neither hydrochloric acid nor sodium hydroxide is capable of entrance into the uninjured cell. If jellyfish are allowed to swim in sea water to which neutral red has been added, they take up the dye into their cells, where it has the orange-red colour of the neutral solution. Bethe (1909) added hydrochloric acid until the colour of the dye in the water was changed to the cherry red of the acid solution. But the contents of the cells underwent no change in colour until enough acid had been added to stop the movements and kill the organisms. Warburg (1910) showed that the colour of neutral red inside the eggs of the sea urchin, which are acid, was unchanged by the addition of sodium hydroxide to the water, but immediately changed to yellow by a small quantity of ammonia.

But, it may be said, no evidence has been given that the electrolytes inside the cell are free to diffuse, even if the membrane allowed them to pass. The fact that the osmotic pressure inside cells is too great to be accounted for except by the presence of small molecules in the free state is indirect proof. Animal cells require, to prevent their swelling and rupture by osmosis, an external solution equivalent to 5·4 per cent. glucose or 0·9 per cent. sodium chloride; that is, a solution of 0·3 molar concentration. The osmotic pressure of this is 6·7 atmospheres. If we take a colloid which has

as great an osmotic pressure as hæmoglobin has, we find, on calculation, that a solution of the necessary molar concentration would be solid. Even congo-red would require to be 21 per cent., a value far exceeding its solubility in water.

Höber (1910–1912) has shown, moreover, that there are free electrolytes present in cells. He made use of two methods. The first was by determining the increase in capacity of a condenser when a conductor is placed between its plates. Red blood corpuscles showed a conductivity about equal to that of deci-normal potassium chloride. The second method depends on the damping of the vibration of a rapidly alternating current in a coil by the presence of a conductor in the axis of the coil. By this method the blood corpuscles had the conductivity of a solution of potassium chloride between 0·1 and 0·4 per cent., muscle between 0·1 and 0·2 per cent. Although the methods are probably not sufficiently sensitive to give exact measurements of the concentration, they show clearly that free electrolytes are actually present.

Another experimental result pointing to the same conclusion may be referred to. When cells are immersed in dilute copper sulphate, alcohol, acetone or aniline, there is a marked increase in the conductivity of the outer solution, as shown by Stiles and Jörgensen (1915 and 1917). The additional ions must have come from the interior of the cells.

Living cells oppose an enormous resistance to the passage of an electrical current and if it were possible to examine them free from external electrolytes, it is probable that they would be found to be non-conductors in respect of currents applied by electrodes external to them. But, if they contain free electrolytes, it seems to the writer that the only satisfactory explanation of inability to conduct electrical currents is that the cell is surrounded by a membrane impermeable to these electrolytes, so that there is no possibility of their conveying charges from one electrode to the other. This phenomenon is shown in an interesting way in the method used by Morse (1914, p. 83) to prepare his copper ferrocyanide cells by electrolytic deposition. As the membrane becomes more perfect, the resistance goes up steadily and may amount, after soaking in water, to a million ohms.

The cell membrane can be deprived of this property, of resistance to the passage of currents, by the action of heat, of anæsthetics and so on. After this treatment the cells conduct currents readily.

We may conclude that, when examined under normal conditions and at rest, living cells are surrounded by a membrane impermeable to most salts, to strong acids and bases, and also, as shown by osmotic experiments, to glucose and to amino-acids. There are, however, certain crystalloids to which the cell appears to be permeable under all conditions. These are urea, ammonium hydroxide and some other ammonium salts, certain dyes of low molecular weight, alcohols, etc. But in some of these cases, it is not clear that no damage has been done to the membrane by the solution applied, a difficulty not always taken into consideration.

But the physiologist will raise an objection. If the membrane is impermeable to glucose and sodium chloride how does the cell ever

obtain these materials for its active processes? The answer is to be obtained from the mode of production of the membrane. If it is composed of materials contained in the protoplasm of the cell it will naturally vary its nature according to the state of the cell, while, being a complex colloidal mixture, it will be easily accessible to the influence of electrolytes. But what actual evidence have we that it may become permeable to electrolytes under any conditions?

Direct proof of such changes under natural conditions is clearly difficult, but Lillie (1913) noticed that the cells of the larva of *Arenicola* when in a state of contraction lost their normal pigment, which is usually in solution in the cell contents. Garmus (1912) found that certain secreting cells became less permeable to dyes under the influence of atropine, more permeable under pilocarpine. The point of these observations is that pilocarpine excites glands to activity; atropine stops their activity. Indirect proofs are more in number. The change of electrical conductivity already referred to is a convenient means of detecting changes of permeability. The egg cell on fertilization increases in conductivity (McClendon, 1910, Gray, 1916), as also does the muscle cell on contraction (McClendon, 1912). The movements of the sensitive plant are usually ascribed to an increase of permeability of the cell membranes of the lower side of the "pulvinus." In this way the cells, which are normally distended owing to the osmotic pressure of certain solutes in their interior, lose these solutes and thus the distension due to their osmotic pressure. Blackman and Paine (1918), however, show that, although there is evidence of a very small escape of electrolytes, it is too small to account for the phenomenon, which can be repeated many times with the tissue immersed in warm water. They consider it more probable that the loss of turgor is due to a sudden decrease in concentration of osmotically active substances in the cell.

The effects of certain agents on the cell, producing a temporary, reversible increase in permeability of the membrane, show how the necessary changes might be produced. The most instructive are those produced by inorganic salts. Ringer (1882) was the first to show that the frog's heart is incapable of continued activity in a pure solution of sodium chloride, even of the correct osmotic concentration, whereas the addition of salts of calcium and of potassium in relatively small amount enabled the beats to continue indefinitely. A large number of experiments on such "balanced solutions" were made by Loeb (1901 and onwards) and brought into relation with changes in the permeability of the cell membrane. The experiments of Osterhout (1911) on the seaweed, *Laminaria*, showed that the tissue increased greatly in electrical conductivity when immersed in a solution equivalent to sea water, but containing sodium chloride only, returning to its normal state on the addition of a certain proportion of calcium chloride. No permanent damage was done to the cells (Osterhout, 1915) by repeating the experiment many times. The explanation given by the investigator himself is not quite clear, but to the present writer it seems to be as follows: As we saw above, the cells in normal conditions are non-conductors because their surface membranes do not permit the passage of ions. Under the influence of sodium ions these mem-

branes become permeable and allow free movement of ions carrying electric charges through them. Calcium ions restore the normal state of semi-permeability. In this connection, the experiments of Clowes (1916), referred to in the preceding section, are significant. We have seen that the constituents of the cell membrane are most probably fatty substances, since they lower surface tension, together with concentrated solutions of emulsoid colloids in water, perhaps in the gel state, but certainly forming a watery phase. In other words, we have a system similar to that of oil and water in the experiments of Clowes, but more complex. Under the influence of sodium salts, Clowes' emulsion was one of oil drops in a continuous watery phase and therefore permeable to water and to solutes therein. On the other hand, under the influence of calcium salts, a phase reversal occurred, so that there was then an emulsion of water drops in a continuous oil phase. Such a system would be impermeable to water, but permeable to substances soluble in oil. A change of this latter kind, if complete, would not give us the properties which the normal cell membrane possesses. It would be impermeable to water, as well as to solutes in water. These solutes would not be able to manifest their osmotic pressure and the volume of the cell would not have any relation to the osmotic pressure of an external solution, as we find that it actually has. Incidentally, however, it appears from some experiments by Lillie (1917), on the changes of permeability in fertilized egg cells, that, under exceptional conditions, the production of a "waterproof" membrane may be possible. But what we have to explain is the change from a membrane permeable to salts, sugar, &c. to one impermeable to them, while remaining permeable to water. It is clear that the "Clowes effect," as we may call it, must be only partially effected. The way in which Bancroft explains the mode in which it takes place is summarized by Clowes as follows:—"The soaps present in the system tend, as stated above, to concentrate at the interface between water and oil and to form a coherent film. Soaps of monovalent cations, being readily dispersed in water but not in oil, form a film or diaphragm which is wetted more readily by water than by oil, consequently the surface tension is lower on the water than on the oil side. Since the area of the inside face of a film surrounding a sphere is obviously smaller than that of the outside face, the film tends to curve so that it encloses globules of oil in water, in this manner reducing the area of the side of higher surface tension to a minimum as compared with that of lower surface tension. On the other hand, a film composed of soaps of divalent or trivalent cations, being freely dispersed in oil but not in water, is wetted more readily by the oil than by the water, the surface tension is lower on the oil than on the water side, and the film tends to curve in such a manner as to enclose the globules of water in an outer or continuous oil phase." The process is dependent on the presence of a film of soap between the phases and it is interesting to note the powerful effect of sodium oleate in destroying the membrane of the red blood corpuscles, while pure olein has not this effect.

During the process of phase reversal, as described above, there is a stage in which one of the two phases is drawn out into elongated

drops with narrow films or channels of the other phase between them. This is shown in Figure 2 of the paper by Clowes. Now, if these pores were small enough, we have the possibility of the production of a membrane with the structure that Traube held that of the copper ferrocyanide membrane to be, namely, a sieve whose holes were of dimensions such that water molecules could pass through, while larger molecules, such as those of calcium chloride or potassium sulphate, could not. Here we meet with the disputed question of the *nature of the semi-permeable* membrane in general. It seems to the writer that the evidence in favour of Traube's original view is very strong, although further evidence on the point is much required. In the case of membranes such as those of parchment paper or collodion, which are permeable to water and the small molecules of crystalloids, impermeable to the large molecules or aggregates of colloids, the degree of permeability appears to be strictly in proportion to the dimensions of the particles of the solutes. In the case of the copper ferrocyanide membrane, some observers hold that the passage of water depends on the different degrees of hydration of the colloid material of the membrane on its two faces. Even Morse (1914, p. 87) appears to hold this view, but the degree of hydration of colloids follows quite a different law from that of osmotic pressure. While the osmotic pressure of a solution is directly proportional to the molar concentration, not the chemical nature of the solute, the hydration by salt solutions follows the series known as that of Hofmeister, where sodium and lithium salts, for example, behave differently from one another. Some investigators, moreover, state that non-electrolytes have no influence on the amount of water taken up by colloids. Objection also may be made to the theory of the production of osmosis by surface tension effects. Surface tension is not a function of molar concentration only, whereas osmotic pressure is. But, however this may be, Tinker's (1916) photographs show a definitely porous structure in the copper ferrocyanide membrane. The measurements given by him of the dimensions of the pores must be received with caution, since the published photographs show obvious diffraction. Indeed, the method of illumination used, a narrow cone of light, is not in agreement with the recognised methods of " critical " illumination, with a wide angled cone, adopted by the microscopists. The conclusions drawn as to adsorption of water molecules on the walls of the pores are also open to question. Further discussion of the problem is beyond the scope of this report, but we have seen how a sieve-like membrane might be formed on the surface of the protoplasm, whereas a membrane which owed its semi-permeable character to its behaviour as a solvent for some solutes and not for others is much more difficult to imagine.

At this place a few words are desirable with respect to the Overton (1899) theory of the membrane as composed of lipoid material. It is a striking fact that the cell membrane is always permeable to those substances which are soluble in fats, such as the alcohols are. But, when we extend this statement and make it to apply generally, we meet with difficulties. For instance, certain dyes, such as methylene-blue, are found to penetrate the cell membrane, while others, aniline-blue, do not. Methylene-blue is insoluble in chloro-

form, but if a solution of kephalin (a lipoid allied to lecithin) in chloroform be shaken with a solution of methylene blue in water, the chloroform phase is found to be coloured blue. In order to understand what this really means, we must refer to the work of Loewe (1912). He shows that kephalin is not in true solution in chloroform, but in large colloidal aggregates, since no measurable change in the boiling point of chloroform is produced by dissolving kephalin in it. The second point brought out is that, when methylene blue is present in the two phases, water and lipoid-chloroform, in contact, if it were a case of true solution in the latter, there would be a definite "partition-coefficient," independent of the absolute concentration. This is not the case. There is relatively *less* in the latter phase as the concentration rises, and the law followed is the parabolic law of adsorption. The actual ratio is such as to involve a high polymerization of the dye in both solvents, whereas electrical conductivity measurements indicate normal molecular weights in water. Again, if the dye were dissolved in the lipoid, a notable proportion of it would escape to water if placed in contact with it. Only a very minute amount leaves the lipoid. In fact, it behaves just like a negatively charged surface such as that of paper in water, to "basic" dyes, which are hydrolyzed in solution, and whose coloured base becomes a positively charged colloidal particle. As Freundlich has pointed out, the adsorption in such cases is so great that equilibrium is only effected when a very small amount of the dye is left in the water. Further confirmation of the view that we have to deal with a surface condensation only is that, if a mass of kephalin be placed in contact with a solution of methylene blue in water, the dye does not pass into the lipoid. Similar evidence was obtained in the cases of other "lipoid-soluble" substances, such as the alkaloids and certain narcotics. It is impossible to accept the view that the cell membrane is a lipoid film, and that the passage of substances into and out of the protoplasm depends on their solubility in lipoids.

It is also easy to show that a membrane of pure protein, as held by some, has not the requisite properties. Nothing but a complex system of more than one phase will suffice to explain the changes in permeability which are shown by the surface membrane of the cell.

We have already spoken of the effect of certain electrolytes on the membrane. Further discussion as to the meaning of "balanced" action will be found in the following section of this report. A few more facts in connection with permeability may be given here. Newton Harvey (1914) was unable to find any general law as to the relation of cells to acids, except that if an acid is soluble in lipoids it penetrates freely; if not, the cell surface must be changed before it can enter. Strong bases do not enter; weak bases do. This fact suggests that the permeability is in respect of one ion only. Since weak bases enter, OH' must do so. Therefore, when sodium hydroxide does not, it must be that the sodium ion is obstructed. This point was indicated by Ostwald (1890). It is sufficient for a membrane to be impermeable to one of the oppositely charged ions of an electrolytically dissociated solute in order that the solute may be completely kept out. The reason

is because the two ions cannot be separated without the expenditure of a large amount of energy on account of electrostatic forces. We shall see presently that this fact plays an important part in the electrical behaviour of living cells.

The action of *anæsthetics* is of interest. Osterhout (1916) has shown that there are two stages in this action, of opposite nature. The first one is a *decrease* in permeability, the second an *increase*. The former is recovered from on removal of the anæsthetic, while the latter is a toxic effect, irreversible and leading to death. Remembering that the characteristic action of anæsthetics is to make a cell unable to enter into a state of excitation, and that the state of excitation is associated with an increase of permeability, we see that the first stage is the real anæsthetic action. Whether the state of excitation is a consequence of the permeability change, or *vice versa*, is not certain, but it may well be that the prevention of the permeability change also removes the possibility of excitation. The pronounced " lipoid-solubility " of the volatile anæsthetics suggests that their action is on the lipoid constituents of the membrane, but magnesium salts have a similar action, so that it seems probable that the relationship to lipoids may be merely incidental.

The interesting observations of Meigs (1915) on the permeability of membranes of colloidal calcium and magnesium phosphates show that such membranes may be impermeable to sugar, phosphates, &c., but highly permeable to ethyl alcohol. Hence this latter property is not limited to " lipoid " membranes.

As pointed out previously, calcium salts decrease, while sodium salts increase the permeability of the cell-membrane, so that the effects may be balanced. Anæsthetics also decrease the permeability. Hence they should oppose the effect of sodium salts. This has been shown by Lillie (1914) to be the case

Since the membrane is a local concentration of components of the protoplasm of the cell, there must always be an equilibrium between the two. Hence a change in either involves a change in both. It is not a matter of surprise, therefore, to find that substances applied to the outside of a cell may effect marked changes in its chemical behaviour, even when they are unable to pass through the membrane. Thus, as mentioned above, sodium hydroxide does not enter the living cell, but it increases greatly the rate of its oxidation processes. Newton Harvey (1914, p. 142) finds that although weak alkalies (ammonia and amines) enter muscle cells almost instantly, as shown by the change in colour of neutral red within the cells, their contraction does not cease until some time later. Strong alkalies (sodium hydroxide) abolish contractile power at once, but do not enter the cell until long afterwards. The effect of electrolytes on the beat of the heart and on muscular contraction in general is on the cell membrane (*see* Straub, 1912, p. 14, and Overton, 1904, p. 202). A somewhat remarkable phenomenon occurs in the case of such drugs as muscarine and pilocarpine, which produce their effects while passing through the membrane in either direction, whether entering or leaving the cell. When in equal concentration on both sides their effect is nil (Straub, 1907, Neukirch, 1912).

In order that the cells of the tissues of the higher animals shall maintain their normal water content and volume, it is necessary that they be surrounded by a solution of the same osmotic pressure as their own contents. The fact that whatever be the chemical nature of the solute, so long as it does not injure the cell, its osmotic pressure must be of the same definite value, unless either swelling or contraction of the cell is to occur, is in itself proof of the semi-permeability of the cell membrane. The facts are so simply explained on this view that it is somewhat puzzling to understand why elaborate theories should be invented to explain the phenomena otherwise. The question naturally arises, nevertheless, how do organisms like amœba, living in water, avoid swelling up and disintegration on account of the osmotic pressure of their contents? We have no accurate knowledge of the value of this osmotic pressure, but we know that it must be higher than that of the extremely dilute solution in which they live. It is pointed out by Stempell (1914) that the well-known *pulsating vacuole* of protozoa is the means of removing excess of water taken in by osmosis. A minute drop of water makes its appearance at a particular place in the protoplasm, gradually increases in size until it touches the outer surface of the organism and bursts to the exterior. The process is continually repeated.

The taking up of *solid particles* and small organisms, such as algæ and bacteria, by living cells, as in the process of ' phagocytosis,' seems at first sight to be difficult to understand. If molecules of sodium chloride are unable to pass through, how do such large masses manage to do so? The writer has suggested in another place (' General Physiology,' p. 144) that the membrane is actually perforated in the latter process, as when a needle is dropped through a soap film, the film closing up again as the object passes through. As we have seen, the cell-membrane is not a fixed structure, and the difference between the impermeability to salts and the permeability to large particles is that in the former case the molecules would have to pass through pores which are too small for them; in the latter case they break the film mechanically, but it is formed again behind them.

It will be of some interest, in conclusion, to refer briefly to some typical physiological phenomena in which membranes of variable permeability are believed to play an essential part. A limited selection is all that is possible, since, as pointed out above, the properties intervene in nearly all vital processes.

I. *The Stimulation of Nerve.* Nernst (1899) was the first to suggest that the electrical stimulation of nerves is conditioned by the concentration of ions of a certain sign of charge in the neighbourhood of a semi-permeable membrane. He made no statement as to the situation of such a membrane, nor did he claim that his theory was more than an approximation. A more complete extension of this theory was made by A. V. Hill (1910) and found by Keith Lucas (1910) to satisfy experimental results. There is no evidence of the existence of membranes within the nerve fibre itself, the contents of which, so far as can be made out, are liquid. Hence the membrane in question must be that on the exterior of the central core, that is, the cell-membrane. The relation of increased permeability to the

condition of excitation has been emphasized by Lillie (1914) and the manner in which it is possible to explain the conduction along a nerve fibre on the basis of the disappearance of the electrical charge described below is explained (1915).

II. *Electromotive Phenomena.* If a membrane is permeable to ions of one sign only, a Helmholtz double layer is established, such that the opposite sides of the membrane obtain opposite charges, owing to the ions held there. In other words, the membrane is polarized. It has been known for many years that muscle and nerve fibres show, on testing, that their outer surfaces have a positive charge. This can be most satisfactorily accounted for on the hypothesis that the cell-membrane is impermeable to certain anions, permeable to the corresponding cations. In the address to the Physiology Section of the British Association in 1915, I showed how this view explains the phenomena met with and may venture to repeat the paragraph here :—

" Suppose that we lead off, to some instrument capable of detecting differences of electrical potential, two places on the outer surface of a cell having the properties referred to. It will be clear that we shall obtain no indication of the presence of the electrical charge, because the two points are equipotential and we cannot get at the interior of the cell without destroying its structure. But if excitation means increased permeability, the double layer will disappear at an excited spot, owing to indiscriminate mixing of both kinds of ions, and we are then practically leading off from the interior of the cell, that is, from the internal component of the double layer, while the unexcited spot is still led off from the outer component. The two contacts are no longer equipotential. Since we find experimentally that a point at rest is electrically positive to an excited one, the outer component must be positive, or the membrane is permeable to certain cations, impermeable to the corresponding anions. Any action on the cell such as would make the membrane permeable-injury—certain chemical agents and so on—would have the same effect as the state of excitation." The point of view taken here is practically identical with that of Bernstein (1913). Loeb (1915) has brought some objections to this view, based mainly on the fact that the application of salts to one of the places led off results in a change of the potential difference of such magnitude as to follow the well-known Nernst formula for concentration cells. I may point out that I have been able to show, both experimentally and by calculation (1911 and ' General Physiology,' pp. 648–650), that one can imitate the muscle cell by means of an osmometer, closed by a parchment paper membrane and filled with a solution of congo-red. This membrane is permeable to the sodium ions resulting from the electrolytic dissociation of the dye, but impermeable to the anions. The only difference is in the sign of the charge on the inside and outside, the latter being negative in this case. The potential difference between the two sides, which can be modified or abolished by the addition to the outer liquid of a solute giving sodium or other cations, is found to be in accordance with the Nernst formula. In fact, a cell of the kind described is a model of the rationale of the electrode potential of the concentration battery. It seems that there is then no real opposition between the results

obtained by Loeb and Beutner (1912) and the hypothesis advocated here. The potential difference between two liquid phases, referred to by Loeb, has clearly the same origin as the membrane potential of the cell. The former has been investigated by Haber and Klemensiewicz (1909) in a well-known paper. If the salt is hydrolytically, as well as electrolytically, dissociated, a more complex state of affairs exists, which has been investigated thermodynamically by Donnan (1911). If, for example, we are dealing with a sodium salt of a weak acid, there are no forces to restrain the free diffusion of sodium hydroxide through the membrane, so that the alkali would be detected on the outer side, while the colloidal acid inside might be precipitated. Moreover, when no hydrolysis is present, if an acid, even as weak as carbonic, is present outside, the sodium ions at the membrane are partially replaced by hydrogen ions, the sodium combines to form carbonate and, by renewal of the outer fluid, all of the sodium can in time be removed.

III. *Secretion.* Although it is clear that complex changes of permeability occur in this process, too little definite knowledge is at hand to make detailed discussion of profit. The reader may be referred to my "General Physiology," pp. 163 and 334, for a brief statement. The point of immediate interest is that, suppose we have an inverted U-tube with a semi-permeable membrane at both ends and filled with a solution of cane sugar. If we immerse both ends in water in two separate vessels, a large osmotic pressure will develop inside the tube, but no liquid will escape, provided that the membranes can withstand the pressure. Now imagine the semi-permeable membrane at one end to become permeable to the sugar. A current of water, carrying sugar in solution, will pass through the tube from one vessel to the other, as long as there is any sugar left in the tube. This tube may be compared to the cells of a secreting gland, one end being in contact with lymph, filtered from the blood, the other end with the watery secretion in the duct. Water can be conveyed in the way described by a change in the permeability of the end bordering on the duct. Cases of this kind have been described by Lepeschkin (1906) in plant mechanisms.

IV. *The Blood Vessels.* Scott (1916) showed that when liquid is absorbed into the blood from the tissue spaces, this liquid, while containing all the crystalloids, is free from the colloids. The walls of the blood vessels are therefore impermeable to colloids. If, then, these colloids are such as have an osmotic pressure, the conditions are such that it can be manifested and it will play an important part in the passage of water from the blood to the tissues, and *vice versa.*

A few words are necessary, therefore, on the osmotic pressure of colloids. Starling (1896) showed that those present in the blood have an osmotic pressure of about 30 to 40 mm. of mercury at room temperature. Later work by Moore and Roaf (1907), Donnan and Harris (1911), Sörensen (1918) and myself (1911) showed that there are many colloids whose active elements are sufficiently small to give a fairly high osmotic pressure. When the colloid is an electrolytically dissociated salt of a diffusible ion with one to which the membrane is impermeable, as in the case of congo-red with a

parchment paper membrane, an interesting question arises, whether the diffusible ions, which are held only by electrostatic forces, play their part in the osmotic pressure. I showed (1911), by determinations of the osmotic pressure of congo-red solutions by a vapour pressure method, that the values were the same as those given by the parchment paper membrane. Therefore, all the elements present in the solution, including the sodium ions, gave their proper contribution to the osmotic pressure measured by the osmometer method; otherwise, the vapour pressure measurements would have been much higher than those with the latter method. Theoretical considerations and calculations based on them (Bayliss, "General Physiology," p. 649) confirm the fact. Owing to the osmotic activity of all the ions formed by an electrolytically dissociated colloid comparatively high osmotic pressures may be manifested. This is the cause of the large rise in osmotic pressure produced by the addition of sodium hydroxide to a protein solution.

In order that we may realize how the osmotic pressure of colloids is of importance in problems of the circulation of the blood it is necessary to remember that the pressure in the arteries is something over 100 mm. of mercury, falling regularly to about 8 mm. in the capillaries, and to zero in the small veins. Since the osmotic pressure of the colloid in the blood is only 40 mm. of mercury, and the walls of the blood vessels are freely permeable to water and crystalloids, it is clear that the osmotic pressure of the colloids, which tends to draw water in, is overpowered as far as the commencement of the capillaries. Thus a filtration outwards of blood, minus its colloids, takes place in that part of the vascular system in which the pressure exceeds 40 mm. The same process occurs in a part of the kidney, resulting in the production of what is a very dilute urine, being the first stage in the complete process. The blood is then continually losing liquid to the tissues up to a certain region in its course. But, as we follow the gradual fall in the blood pressure along the capillaries, we come to a point where the osmotic pressure of the colloids, which has risen somewhat owing to the loss of water, is higher than the blood pressure. From this point onwards water is taken in again from the tissue spaces by osmosis. This latter process, however, does not usually suffice to balance the loss completely, and the difference is carried away by the lymphatic channels, and finally returned to the blood by the thoracic duct. Consider next what will happen when a dilute salt solution is introduced into the veins in order to replace blood which has been lost by escape from injured blood vessels for example. It is clear that the concentration of colloids in the blood is lowered, and therefore their osmotic pressure. The result is that more rapid loss of liquid by filtration occurs, while the region travelled before the blood pressure falls sufficiently to permit osmotic inflow is lengthened, leaving a less distance in which reabsorption takes place. The net effect is that much more liquid escapes to the tissues, while the blood quickly loses that which has been put in. In practice this is found to be the case. Simple saline solutions are useless. The present writer has shown (1916), however, that if a colloid, such as gelatin, or better, gum acacia, be added in such amount to the solution injected as to raise its colloidal osmotic

pressure to that of the blood, then it remains in the blood vessels raising the blood pressure and forming an effective substitute for the blood lost. Indeed, a gum solution of this kind was in extensive use during the war.

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III. The Relation of Biochemical Colloids to Electrolytes.

We have already met with several instances in which the interaction between colloids and electrolytes plays an important part. In the present section, further analysis of such phenomena will be attempted.

It is necessary to take account of the fact that the greater number of the colloids occurring in living organisms are proteins. These, being conjugated amino-acids, behave as amphoteric electrolytes, able to combine with strong acids by their NH_2 groups and with strong bases by their carboxyl groups. Electrolytically dissociated salts are thus formed, the protein ion being the cation in the former case, the anion in the latter. Although there is no doubt of this fact, it is sometimes forgotten that the protein itself is present in solution in the form of an anhydride, the NH_2 and COOH groups are not free to combine with ions until hydrolyzed by the action of strong acids or bases. Nevertheless, various statements have been made to the effect that not only are chemical compounds formed with weak acids, but even with neutral salts. That this is not so is shown clearly by the results of Bugarsky and Liebermann (1898), who found no change in the freezing point on adding egg albumin to sodium chloride, whereas there was a marked depression with hydrochloric acid or sodium hydroxide. The evidence brought by Pfeiffer and Modelski (1912), to the effect that amino-acids form definite chemical compounds with calcium and lithium chlorides and other salts, is not convincing and the present writer was unable to confirm their statements.

Hardy (1905–6) finds that globulins form non-ionized complexes with neutral salts. On the other hand, Loeb (1918) holds that neutral salts with a univalent cation form highly ionizable salts with gelatin. The evidence is that powdered gelatin, after washing with m/8 or m/4 solution of sodium chloride, shows a further swelling when afterwards put in contact with a more dilute solution of a neutral salt with a univalent metal. There is a critical concentration above which this additional swelling is absent. And this concentration is half as great if the anion is bivalent, regardless of the nature of the anion and cation. The evidence is somewhat indirect, but it indicates an electrical effect independent of the

chemical nature of the ion. Whether the conclusion is justified that it implies the production of a definite salt seems doubtful. The difference between the osmotic pressures of equimolar solutions of sodium salts with uni-and bivalent anions must not be forgotten. A further difficulty is presented by the fact that calcium salts were not found to form ionizable compounds, whereas in the experiments of Pfeiffer and Modelski (1912), the " compounds " of amino-acids with calcium chloride were some of the easiest to prepare. If the contrast is due to the colloidal nature of gelatin, it is an additional reason to doubt the adequacy of explanation on pure electro-chemical lines. Why does Loeb speak of proteins as " so-called colloids " ?

If a salt of a protein with a strong base or strong acid is exposed to an electric field between electrodes, the colloidal ion is deposited at one pole or the other according to whether it is anion or cation and the protein is naturally said to have a charge of the sign opposite to that of the pole at which it is deposited. But the sign of the charge on such a surface as that of paper can be changed by electrolytes, even by weak acids and by neutral salts. In such cases, it seems that something other than actual salt formation must be the cause. Whatever may be the way in which the electric charge on the surface of insoluble particles or colloids is produced, whether by electrolytic dissociation at the surface, one ion being insoluble and fixed (see Hardy, 1910), or by other causes more allied to the phenomena of static electricity (Lewis, 1909), as appears to be the case with drops of petroleum in water, it is clear that the surface energy due to this charge would be reduced if ions of the opposite sign were deposited on it. The second law of thermodynamics would allow us to predict this fact, which has been called " electrical adsorption." It is shown in a striking way by the opposite effect of bivalent ions on the adsorption of colloidal dye ions by paper, when these have a different sign of charge. Some data on this point will be found in a paper by myself (1906). I was inclined to attribute the effect to a reversal in sign of the charge on the colloidal particles, but it is more satisfactorily explained as exerted on the paper. While, however, it is comparatively easy to see why the charge should be reduced to zero, it is not quite so easy to see why it should be replaced by a charge of the opposite sign, as Perrin (1904, 1905), Mines (1912) and others have shown to be the case. Freundlich (1909, p. 245) has suggested that certain ions may be adsorbed in the mechanical way to a much greater extent than certain others with an opposite charge. The result would be a deposition on the surface in amount greater than merely necessary to neutralize the existing charge and sufficient to confer a charge of the opposite sign. (See specially the experiments of Freundlich and Schucht, 1913, and of Hizaka, 1913.)

We have, then, in addition to the chemical compounds of certain amphoteric electrolytes with strong acids and bases, as association of electrolytes with the surfaces of colloids in general, a relationship which appears to be of the nature of adsorption. This is indicated by the law which expresses the proportion of electrolyte held by the colloid to that in the external phase. The law is expressed by the equation to one of the higher orders of parabolas. This is the reason

why it is so difficult to remove, by repeated changes of water or dialysis, the last traces of electrolytes attached to colloids or coarsely heterogeneous systems.

This difficulty of removing all electrolytes and other crystalloids from a colloidal solution has led some workers in the past to the belief that the osmotic pressure shown by some of these solutions was due to the electrolytes present. There are several reasons, theoretical and experimental, that make this view inadmissible. In many cases, such as gelatin and congo-red, the more effectively these impurities are removed, the higher is the osmotic pressure. If the crystalloid is in any form of combination with the colloidal particle, chemical or by adsorption, it forms one indivisible system with it, so that if a colloidal particle is too large to possess the kinetic energy requisite to give an osmotic pressure, it would be even less able to do so if attached to another molecule. In fact, the association of a colloidal particle with an electrolyte would decrease the osmotic pressure given by it. If, on the other hand, the electrolytes are free, they must be removed by repeated dialysis. The osmotic pressure of hæmoglobin (Hüfner and Gansser, 1907) is that which it should have in accordance with its molecular weight as determined by chemical analysis. It is true that certain colloids, such as ferric hydroxide, become unstable if the last traces of ferric chloride are removed, but the particle consists of a complex of a variable number of ferric hydroxide molecules in adsorption with one or more ferric chloride molecules. The latter are not free.

The greater number of the colloids of biochemical interest belong to the class called *emulsoids*. Their characteristic is that the two phases are not solid and liquid, but both contain solvent in different amounts. The two phases in these biochemical colloids may be described as being, on the one hand, a solution of a small amount of the solvent in the solid, and, on the other hand, a dilute solution of the solid in the solvent. They may also be regarded as being both liquid, one of them possessed of a very high degree of viscosity. Such systems would not show a high surface tension at the interface, nor a high electrical charge. They are, accordingly, relatively to the suspensoid class, somewhat insensitive to the precipitating action of ions. At the same time, as Mines has shown (1912, p. 211), the difference is not a fundamental one and is merely one of degree. Egg white is at once thrown down by a simple trivalent ion, such as lanthanum, even in a concentration of only 0·0016 molar. The complex trivalent ion of the luteo-cobalt salts (Mines, 1912) does not precipitate emulsoids, although it is nearly as effective on suspensoids as the simple lanthanum ion. The fact appears to be related to the low density of the charge on the large ion.

On the other hand, these particular emulsoid colloids react in an important way to another property of salts, that property called by Freundlich (1909, pp. 54 and 412) "*lyotropic*." It is manifested by changes in the distribution of the solvent between the two phases, dependent on changes in the solvent itself. In the case of water, we speak of the hydration of the ions and changes in the equilibrium between the various states of water itself. These give rise to alterations in the internal pressure, compressibility, viscosity, solubility, &c.

The phenomena are not in relation to the valency of either ion, but follow a series known as that of Hofmeister (1888). The order of activity in anions is:—

$$SCN < I < ClO_3 < NO_3 < Cl < CH_3COO < SO_4 < \text{tart.} < \text{citrat.}$$

In cations:—

$$NH_4 < Li < Cs < Na < Rb < K.$$

But the difference between individual cations is less marked than that between anions. This series is met with in many phenomena in which emulsoid colloids play a part. The action appears to be preceded by adsorption.

The effect of acid and alkali in increasing the amount of water taken up in the swelling of emulsoid colloids has been the subject of experiments by Martin Fischer and G. Moore (1907), Chiari (1911) and others. According to Pauli (1912), the swelling is due to the formation of electrolytically dissociated salts and the affinity of the protein or other colloidal ion for water. If this be the case, we see how little importance the process can have in the phenomena of œdema or of "acidosis," where the possible increase in hydrogen-ion concentration is far too small to result in any salt formation with proteins. The experimental results of Fischer and Moore show, moreover, that a fairly high degree of acidity is necessary to produce any significant effect. Pauli's point of view is rendered doubtful also by the fact that the swelling occurs in solids, as well as dispersed molecules. It seems more likely that it is due to a change in the properties of water at the surfaces of the constituent elements of the colloidal masses, a change conditioned by the adsorption of inorganic ions at this situation.

The opposite effects which sodium and calcium salts have in reversing the phases of oil and water systems and on the permeability of the cell membrane have been referred to in the preceding section, together with the necessity for the presence of both for maintenance of the normal cell processes. If we confine our attention only to the cation in its action on emulsoid systems, it is difficult to understand why there should be, not merely a quantitative difference between univalent and bivalent ions, but an opposite effect. Clowes (1916, p. 408) holds that the opposition is really one between anions and cations, a more intelligible view. In the case of calcium chloride, for example, the cation is more powerfully adsorbed and reactive than the anion; in that of sodium chloride, the anion is adsorbed to a greater degree than the cation. Hence the possibility of obtaining a balance between the two effects and the reason why a small concentration of calcium chloride balances a much larger one of sodium chloride. This view is confirmed by the fact that much less sodium citrate than of sodium chloride is required to counteract the effect of calcium chloride, because the citric anion is more powerfully adsorbed than the chlorine ion. But the possibility of the production of complex ions, containing calcium and the citric ion, must not be overlooked.

A certain difficulty arises with regard to potassium. It is found that to maintain normal cell processes and to permit growth the presence of a small concentration of potassium salt is necessary in

addition to that of sodium and calcium. We may perhaps be satisfied with the statement that potassium is required on account of particular chemical properties. This appears to be the view taken by Loeb and Cattell (1915), but, as we have no idea as to what these properties are, very little is gained. Some recent work by Zwaardemaker (1918) is of importance with respect to the elucidation of the problem. This observer noticed that the elements which Ringer found to be able to replace potassium, namely, rubidium and caesium, are, like potassium, weakly radio-active, and he proceeded to test other substances more powerfully radio active, such as radium itself, emanation, uranium, and thorium. It was found that equally radio-active concentrations of all the elements named were equal in their capacity of replacing potassium in a solution adequate to maintain normal cell life.

Sodium salts are chosen to make up the correct osmotic pressure of these fluids because they are the least toxic salts. But Clark (1913, p. 77) found that a better solution was obtained if a part of the sodium chloride was replaced by its osmotic equivalent in cane-sugar.

Some very interesting conclusions have been drawn by Macallum (1904) from the fact that the salts present in sea water form an appropriately balanced mixture for the cells of the higher vertebrates, when the sea water is diluted to the correct osmotic concentration. It seems evident that the electrolyte composition of the blood of the present land vertebrate is that of the ocean at the close of the Cambrian period, when their ancestors left the water and took to the land. The Cambrian period was an extremely long one and the colloidal systems of the cell were developed in adjustment to this balanced mixture of salts. But at the same time, it is a remarkable fact that the particular mixture arising from the dissolving of constituents of the earth's surface should be that of a "balanced" solution, not only for protoplasm, but also for emulsions of oil and water.

There is another interesting way in which the relationship of colloids to electrolytes meets us in physiological phenomena, namely, the mechanism of *muscular contraction*. Blix (1891) and A. V. Hill (1913) have shown conclusively that the tension developed is proportional to the area of certain surfaces arranged longitudinally in the muscle and is not a volume effect. Fitzgerald (1878) and Bernstein (1901) had already suggested surface tension at the contact between the fibrillæ and sarcoplasm as the mode of production of the muscular force, and there are other facts which confirm the view that surface phenomena form a component part of the complex of events. Surface tension has the peculiarity of possessing a negative temperature coefficient, doubtless connected with the absence of any boundary surface at the critical temperature. The contractile stress produced by muscle has a negative temperature coefficient (Bernstein, 1908), as also has the heat produced in the initial stage. Lactic acid is one of the chemical products of the muscular process, and Haber and Klemensiewicz (1909) put forward the hypothesis that the acid alters the electrical forces at the boundary between the fibrillæ and the sarcoplasmic liquid. This again involves a change of

surface tension, which brings about the mechanical shortening of the fibres. The negative temperature coefficient excludes swelling of colloidal fibrils under the influence of acid as accounting for the muscle process as suggested by some. The imbibition of water has a positive coefficient.

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IV. Enzymes.

In the present report, that aspect only of the action of enzymes which is related to their colloidal nature will be discussed.

The fact that enzymes are present in their solutions in the colloidal state is shown by their non-diffusibility through parchment paper, and is now generally recognized. Taking this fact into consideration, together with the form of the relation between the concentration of the substrate and enzyme and the velocity of the reaction, the present writer (1906) put forward the hypothesis that the chemical decomposition of the substrate is preceded and controlled in rate by adsorption. Not only, however, are enzymes in the colloidal state, but they are able to act in a medium in which they are insoluble and present as coarse particles which can be filtered off, leaving the filtrate inactive. This has been shown in the case of lipase by Dietz (1907), in that of emulsin by Bourquelot et Bridel (1913), by myself (1915) for lactase, papain, peroxidase, catalase, urease, and invertase, with great probability for trypsin and pepsin. Armstrong, Benjamin and Horton (1913) came to the conclusion that urease acts by its surface. A similar conclusion may be drawn from the fact that invertase may be adsorbed by charcoal and nevertheless remain active (Nelson and Griffin, 1916). We may conclude, then, that enzymes belong to the class of catalysts present as a separate phase and acting in a heterogeneous system.

The next question that arises concerns the mechanism of their action.

There are two theories of catalysis in heterogeneous systems: one of these assumes the formation of an intermediate unstable chemical compound between the catalyst and substrate, the reaction following the ordinary laws of mass action; the other regards the chemical change as being brought about, or rather greatly accelerated by close approximation of the reacting substances by condensation on the surface of the catalyst by adsorption. An intermediate position is taken by those who regard the rate of the reaction as conditioned by the amount of reagents present on the surface at any given time, but hold that the actual chemical change is due to formation of a chemical compound with the substance of the catalyst itself, occurring as a second stage of the complete process. This process may be expressed as made up, in order, of adsorption, combination with enzyme, decomposition of intermediate compound, with enzyme left finally as at first.

As a typical instance of the first view, we may take Van Slyke and Cullen's (1914) account of the kinetics of urease. These observers state that the action consists of two consecutive reactions: (1) combination of enzyme with urea, and (2) breaking up of the compound, the urea being freed in the form of ammonia and carbon dioxide. They formulate an expression of two factors, each with an

empirical constant, which, by proper choice of the two constants, satisfies the experimental data. This fact, however, does not prove that the first stage is a chemical combination. Indeed, it is stated that the first stage, combination between enzyme and urea, is so rapid that no appreciable time is lost. If this be so, it is difficult to see why it appears in the equation at all. The authors seem to hold that physical phenomena, such as adsorption, diffusion and so on, follow indefinite laws only, in contradistinction to those of chemical combination. Further remarks with reference to formulae based on mass action alone, will be found below. Although the work in question is the most clearly expressed statement of the particular point of view, the theory itself is probably the most widely accepted one as applying to enzymes. Incidentally, we may remark that the fact that a particular reaction appears to follow the ordinary unimolecular law of velocity, deduced from mass action, is no guide to the nature of the process as a whole. Denham's (1910) reaction, in which a sheet of platinum is the catalyst, follows this law.

For the first statement of the other view, we must go back to Faraday (1834). The experiments and conclusions to be found in his paper, ' On the Power of Metals and other Solids to Induce the Combination of Gaseous Bodies,' are apt to be forgotten, so that I make no excuse for referring to them in some detail. The phenomena in question are the combination of oxygen (and nitrous oxide) with hydrogen, induced by the surface of metallic platinum and other solids. In paragraph 619, Faraday states ' All the phenomena connected with this subject press upon my mind the conviction that they are dependent upon the *natural conditions* of gaseous elasticity, combined with the exertion of that attractive force possessed by many bodies, especially those which are solid, in an eminent degree, and probably belonging to all; by which they are drawn into association more or less close, without at the same time undergoing chemical combination, though often assuming the condition of adhesion; and which occasionally leads, under very favourable circumstances, as in the present instance, to the combination of bodies simultaneously subjected to this attraction.' That the phenomena are regarded as a condensation *on* the surface, not a solution in the substance of the solid, is clear from the reference to hygrometric bodies which ' condense water vapour around or upon their surface,' and are said to be instances of the same power (par. 621). The absence of chemical combination with the surface is stated clearly in par. 631, ' The platina is not considered as causing the combination of any particles with itself, but only associating them closely around it; and the compressed particles are as free to move from the platina, being replaced by other particles, as a portion of dense air upon the surface of the globe, or at the bottom of a deep mine, is free to move, by the slightest impulse into the upper and rarer parts of the atmosphere. Par. 632 calls attention to a fact which is common to adsorption phenomena in general, and is of importance in certain effects of retarding agents on enzymes, as we shall see presently. ' It can hardly be necessary to give any reasons why platina does not show this effect under ordinary circumstances. It is then not sufficiently clean (617), and the gases are prevented

from touching it, and suffering that degree of effect which is needful to commence their combination at common temperatures, and which they can only experience at its surface. In fact, the very power which causes the combination of oxygen and hydrogen is competent, under the usual casual exposure of platina, to condense extraneous matters upon its surface, which, soiling it, take away for the time its power of combining oxygen and hydrogen, by preventing their contact with it ' (598). Numerous facts are described which show that the only condition necessary is a perfectly clean surface, however produced. One way of doing this is of theoretical importance as showing that the action is not due to chemical combination of either oxygen or hydrogen with platinum. Platinum can be made active by making it either anode or cathode of an electrolytic cell (617). Chemical action is also excluded by the fact that nitrous oxide and hydrogen can be made to combine (572), and also by the fact that the ' effect is produced by most, if not all, solid bodies ' in varying degree (618). It may be said that gas reactions only are contemplated in this theory, but statements in pars. 623, 625, and 657 indicate that Faraday had in mind the possibility of similar reactions in liquids. Indeed, the following statement is remarkably like an anticipation of Van Hoff's theory of solutions, 'An analogy in condition exists between the parts of a body in solution and those of a body in the vaporous or gaseous state.'

Denham (1910) brings powerful evidence in support of this theory of catalysis in inorganic heterogeneous systems as being due to the high surface concentration caused by molecular forces at the surface, and the high velocity of reaction as being due to the increased mass action thus brought into play. Bancroft (1918) gives a valuable discussion of contact catalysis.

Denham, however, although he is of the opinion that some enzyme effects may be accounted for in a similar way, hesitates to apply the theory to all enzymes. We may, therefore, proceed to examine the evidence bearing on the question. But before doing this, we should remember that it is possible, as Hardy points out (see paper by Drury, 1914), that there may be, in addition to the simple mass effect, an increased chemical potential of the reacting molecules brought about by the actual process of condensation itself and the stresses which it involves.

That the rate of reaction is controlled by adsorption is evident from various facts. The law expressing the way in which the concentration of enzyme and of substrate is related to the rate of change is not one that could be deduced from mass action. Up to a particular concentration of substrate, which varies with different enzymes, the law followed is that of a parabolic curve, similar to that of adsorption, although this, of course, does not in itself prove that we have to do with adsorption. Beyond this particular concentration, the rate is either constant, whatever the concentration of the substrate, or owing to some secondary effects of the enzyme, is actually diminished. This fact is easily accounted for by the familiar fact that a surface may become saturated; so that, above a certain concentration of the substrate, no more can be adsorbed at a given moment of time. On other hypotheses explanation is

very difficult. Data showing the fact in the case of enzymes are numerous; those of Frankland Armstrong (1904) with lactase may be particularly mentioned.

When attempts are made to express in mathematical formulae the velocity of reaction with enzymes, starting with the usual expressions based on mass action, it is found that numerous empirical factors have to be introduced in order to obtain adequate expressions. Since we do not know the meaning of these factors, it seems to the writer that very little is gained by such procedures. The difficulty is to know exactly what is the active mass at any moment. It is clearly some function of the concentration of the substrate, because this determines the amount adsorbed, but it is also related to the adsorbing capacity of the enzyme surface, which is itself affected by numerous influences, probably changing during the progress of the reaction itself.

According to the theory of Nernst concerning reactions in heterogeneous systems, there are three stages—diffusion of the reagents to the surface, adsorption on this surface, and finally chemical reaction with each other or with the constituents of the surface itself. The stage of adsorption is very rapid when the reagents have reached the surface; so that, since the rate of the reaction as a whole is that of its slowest component, the process of adsorption itself does not control it. When one of the phases is a large mass, the time taken for the reagents to diffuse to it is an important component and usually longer than the actual chemical reaction itself. In such cases, the temperature coefficient of the reaction as a whole is that of diffusion, and is a low one. In the case of a colloidal dispersion, such as an enzyme in solution, the solid phase is evenly distributed throughout the system, so that the paths travelled by the substrate to reach the surfaces of the enzyme particles are very short, and the rate of the reaction is that of the chemical component, with the temperature coefficient of a chemical reaction. It seems likely that the coarsely heterogeneous systems of urease or emulsin in alcohol would be found to have the temperature coefficient of diffusion, but they have not been investigated from this point of view. The failure to realize these various facts has led to confusion of statements regarding the impossibility of an adsorption process having the high temperature coefficient of a chemical reaction. The temperature coefficient of an enzyme reaction is naturally that of whatever chemical change occurs, and it gives us no information as to the other components of the total process.

We know from numerous investigations that when a substance is strongly adsorbed it is capable of displacing another substance to a greater or less degree from its position on the surface. Many of the substances found to retard the rate of enzyme action are of this kind. The alcohols, urethane, saponin and so on lower surface energy markedly. It was natural, therefore, that Meyerhof (1914) should suggest this as an explanation of their action, which was found in a series of related compounds to follow their capacities of lowering surface tension. It is complicated, however, by some other properties of these agents to be referred to below. As was pointed out

in the preceding report in connection with muscular contraction, surface energy is peculiar in having a negative temperature coefficient. If the inhibiting effect produced by saponin, etc., has the cause suggested it should be found to be greater at a low temperature, just as the degree of adsorption in general is well known to be greater at a low temperature. The present writer (1918) in experiments with saponin and with amyl alcohol showed that this actually was the case.

A practical point of interest is the effect of alcohol on digestion. As far as the rate of action of the digestive enzymes on food is concerned all experimental evidence shows it to be a retarding one, and the reason is doubtless that given above.

Remembering that the action of enzymes is a surface one it is clear that any agents affecting the *state of dispersion* must affect the intensity of action. Any agent which increases the degree of dispersion increases the total surface and hence the activity of the enzyme. This factor comes in to complicate the case discussed above, since agents lowering surface tension tend to increase dispersion and thus to counteract the inhibiting effect. A particularly marked case is the accelerating effect of bile salts on the action of lipase. It was thought to be due to better emulsification of the oil used as substrate until it was found to be present also when soluble esters, such as ethyl acetate, were used. It seems, therefore, that it must be due in part to greater dispersion of the enzyme itself.

The possibilities of complexity of action are obviously greater in the *action of electrolytes*, because we have in addition the intervention of electrical forces and the effects of electrical adsorption. Some of these may decrease, others increase, the state of dispersion, according to the sign of charge on the enzyme particles. In the investigation of the effects of substances added to solutions of enzymes we have then a multiplicity of factors to take into account, so that analysis of the phenomena is very difficult and much further work is required. The experiments of Onodera (1915) are of interest in this connection.

We may regard it as established that adsorption of substrate by enzyme particles is the controlling factor in the velocity of the chemical reaction that follows. But is this adsorption followed by chemical combination with the enzyme, forming an intermediate compound of an unstable nature which then breaks up into products different from those substances from which it was formed? In the majority of cases, the chemical change involved is one by which the elements of water are either added or removed, but this is not always the case. There is every reason to regard the effect of an enzyme as an acceleration of the rate at which a given system attains its equilibrium position, the final products being the same as those which would have been formed, very slowly, in the absence of the enzyme. There is no inherent difficulty in the view that the concentration on the surface results in the rapid attainment of equilibrium by increased mass action, in the same way as Faraday explained the platinum effect and as Denham regards the inorganic heterogeneous catalysts in general to produce their results. This

last observer points out that there is only one case in which evidence of a kind of intermediate compound of a chemical nature has been brought forward. So far as I am aware, no compound between enzyme and substrate has been shown to exist. Adsorption compounds or colloidal complexes have been obtained when the substrate is in the colloidal state, as between starch and amylase, and between trypsin and casein. But such compounds are formed whether the substrate is one capable of attack by the enzyme or not. Thus, amylase forms a similar compound with casein and with starch, and it appears to be a mere physical juxtaposition of the colloidal particles, held together by mechanical or electrical forces.

A certain amount of evidence that adsorption alone can increase the rate of change is afforded by some experiments which the present writer made with powdered charcoal and urea solution. Urea in solution, as Walker and Hambly (1895) showed, is slowly changed into ammonium cyanate, up to a certain equilibrium position. This is followed by a further change into ammonium carbonate. The rate of this change is accelerated to a marked degree by the presence of powdered charcoal.

The absence of an intermediate compound is more definitely indicated in the investigation of Horace Brown (1914) on some Cape wines, where an oxidation proceeds under the influence of a catalyst consisting of iron in the ferrous state associated with tannin and protein. This acts as a 'carrier of oxygen,' as in Fenton's reaction. The observations of Moore and Webster (1918) on the photosynthesis of formaldehyde in presence of inorganic colloids are also to the point. They show that the effects are not due to changes of the catalyst from a higher to a lower oxide, but to a surface condensation of carbon dioxide on the particles. The effect is given indeed by silicic acid, in addition to ferric and uranic hydroxides and beryllium chloride, also, to a less extent, by copper, nickel, palladium, manganese and erbium salts. The bearing of this fact on the problem of chlorophyll assimilation in plants is obvious. It suggests that the function of the pigment in the chloroplasts is to absorb light energy which is then utilized by the aid of an iron catalyst to reduce carbonic acid to formaldehyde.

It has been pointed out to me by Prof. Hopkins that if the process is to be regarded as the rapid attainment of the natural equilibrium in consequence of condensation on the surface of the enzyme, it follows that all the constituents of the system must be adsorbed in the same relative proportion as in the body of the liquid, otherwise there must be a change in the equilibrium position. I have made some experiments to test this deduction, but the difficulties are great and the work is for the present interrupted. I found, however, that a mixture of ethyl alcohol, acetic acid, ethyl acetate and water, after equilibrium had taken place, was unaltered by the addition of powdered charcoal although charcoal is known to adsorb some of the constituents, at all events. The result indicates that the various constituents must have been adsorbed in the same proportion as that in which they were present in the mixture. But further experiments are desirable and it does not follow that

enzymes behave like charcoal. Curiously enough, it appears to be well established that, in the case of esters at least, the equilibrium position is not the same with acid as catalyst as with lipase (Dietz, 1907). In the former case, the equilibrium is with 85·5 per cent. ester (amyl butyrate); in the latter, with 75 per cent. ester. The equilibrium is a genuine one in both cases, since it can be reached from either direction. If water were more highly adsorbed from this mixture than the other constituents, the result, which shows more hydrolysis than in the case of acid, might be explained. The fact has given rise to many conjectures, on account of the fact that it seems to give an opportunity to evade the second law of thermodynamics. The considerations given above add yet another, namely, that the fact may be due to unequal adsorption. Whether the equilibrium on the surface of enzymes is of necessity the same as that in the body of the solution is not yet quite clear and this point requires investigation. At any rate, there seem to be no inherent difficulties in the hypothesis suggested. The relative degree of adsorption of the various constituents of a mixture has received some attention, especially by Arrhenius and others working with him (see Williams, 1913). It is clear that all are adsorbed, including the solvent itself.

Some interesting possibilities are pointed out by Bancroft (1918). If different products can be obtained from a particular substance, it may happen that one catalyst adsorbs certain of them more powerfully than another one does, so that the resulting equilibrium may not be the same in the two cases. Similarly, different catalysts, such as platinum, charcoal, clay, etc., may cause different forms of combination in a mixture of gases, according to their relative adsorption. If one of the products of a reaction is very strongly adsorbed, it may possess the surface to such an extent as to stop further action and produce a false appearance of equilibrium, the position of which will depend on the concentration of the catalyst, contrary to the true equilibrium.

The question of synthesis by enzymes does not properly belong to the scope of this report, but it is clear that, since the characteristic of catalysis is the rapid attainment of a natural equilibrium, depending on the relative concentration of the components of the system, the same enzyme will exhibit either hydrolytic or synthetic activity according to the composition of the mixture. Synthetic action requires a low concentration of water (see especially Armstrong and Gosney, 1914), so that, as pointed out previously, a method is wanted by which the cell can vary the effective concentration of water. No special synthesizing enzymes are called for. The evidence that has been brought for the existence of such agents is not convincing (see Bayliss, 1913).

The chief difficulty in regarding the mode of action of enzymes as consisting merely in a surface condensation of the constituents of the reacting system is the apparently specific nature of these catalysts, although the degree of specificity is probably exaggerated. We must remember that the nature of the surface determines adsorption, since all the physical properties of a substance depend on its chemical nature. The possibilities of different adsorption

properties are enormous and the study of the subject is yet in its infancy. One of the most interesting cases of this specific action is that of those enzymes which act on optically active compounds and the synthesis of such compounds by optically active catalysts (see Bredig and Fajans, 1898, and Bredig and Fiske, 1912).

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V. The Transport of Gases in Animals.

Oxygen is continually being used up and carbon dioxide produced by the oxidation of food materials in the tissues of animals. When the current of blood flowing in a given time is compared with the consumption of oxygen and the carbon dioxide produced in the same time it is clear that, in neither case, is the amount that could be carried in solution in the liquid of the blood nearly sufficient to account for that actually transported.

Both these gases, therefore, must be carried in some kind of combination with substances present in the blood. It will clear the way if we exclude certain possibilities at once. Oxygen is taken up by the blood in the air sacs of the lungs, where its partial pressure is about 100 mm. of mercury. The venous blood has an oxygen tension of about 37 mm. of mercury. Accordingly, the substance serving for the transport of oxygen must be one which takes up oxygen when exposed to a tension of this gas of 100 mm. and gives it off again, more or less completely, at 37 mm. or thereabouts. The tension of carbon dioxide in the lungs is 40 mm. of mercury; in the blood arriving from the tissues about 64 mm. or thereabouts. The substance transporting this gas must be one that takes up carbon dioxide at 64 mm. and gives it off at 40 mm. There is only one substance present in the blood that has the requisite properties as regards oxygen, that is the red colouring matter of the red blood corpuscles, hæmoglobin. This has been known for a long time. But some confusion has arisen with regard to carbon dioxide, because sodium bicarbonate is present in the blood plasma, and it was natural to look upon this as the carrier. Bohr (1891), however, had already shown that sodium bicarbonate gives off no carbon dioxide to the gas at a pressure of 40 mm. of mercury, and Buckmaster (1917) has confirmed this statement. The latter observer has also shown that there is no substance present in the blood acting as an acid to drive off the carbon dioxide. There seems to be no possibility of a dissociable compound of carbon dioxide with the proteins of the blood plasma. We have seen that proteins do not combine with weak acids, although a process akin to adsorption may occur, although it is not definitely shown to be present. The part played by the proteins is as yet somewhat uncertain, but the work of Buckmaster has proved that by far the greater part of the carbon dioxide, if not all, is carried by the hæmoglobin in a manner similar to that in which it carries oxygen.

The function of the sodium bicarbonate, as Lawrence Henderson (1908) has so well shown, is to preserve the hydrogen-ion concentration of the blood within narrow limits.

The work of Barcroft and his coadjutors has brought out in detail the relations between oxygen and hæmoglobin, under various conditions, and shown how the facts can be expressed in a mathematical form. A complete account will be found in Barcroft's book (1914). The object of the present report is to point out the difficulties met with when an attempt is made to reconcile the interpretation sometimes given to these expressions with the fact that hæmoglobin exists in the blood as a heterogeneous phase. In the corpuscles the concentration of hæmoglobin is about 30 per cent. No solution of

hæmoglobin of this strength can be made. Even in 5 per cent. it forms a colloidal suspension, and it does not diffuse through parchment paper, however dilute the solution may be.

Barcroft explains the phenomena on the basis of chemical combination between oxygen and hæmoglobin, a series of compounds, HbO_2, Hb_2O_4, Hb_3O_6, &c., being formed in different relative proportions according to the electrolytes present in the solution. These electrolytes are regarded as causing aggregation of hæmoglobin molecules; the aggregate Hb_2, when it combines with two molecules of oxygen, leads, by mass action, to a different order of equation from that of Hb and O_2, which is unimolecular. But it is not yet certain that we are justified in applying the law of mass action in a simple form to heterogeneous systems and, if we apply the phase rule, we are at once met with difficulties, as will be seen below. On the other hand, it is not universally accepted that the phase rule can be applied to colloidal solutions, although the hæmoglobin in the corpuscles may reasonably be regarded as a more definitely distinct phase.

Barcroft's experimental results are of so much value that it seems to the writer that there is some risk of the problem being prematurely considered to be solved and the very remarkable character of the phenomena being overlooked.

Assuming that the phase rule applies, what does it tell us? If HbO_2 is a chemical compound, there are three phases present in a solution of it when in contact with an oxygen atmosphere, Hb, HbO_2 and oxygen. There are two components; because Hb and HbO_2 vary inversely; the oxygen is present in unlimited amount. There is therefore only one degree of freedom:

$$F = C + 2 - P = 2 + 2 - 3 = 1.$$

In other words, at a given temperature, say that of the blood, the *whole* of the hæmoglobin is either reduced or oxidised, according to the tension of the oxygen. But this is not the case. It is well known that hæmoglobin varies in its content in oxygen, at the same temperature, according to the tension of oxygen. It is free from oxygen at zero tension and saturated at about 100 mm. of mercury at the temperature of 38° C., while it follows a particular law, expressed by the dissociation curve, between these values.

Apart from this deduction from the phase rule, there are certain chemical systems that have been hastily assumed to be similar to that of oxygen and hæmoglobin. We shall see that they are different and really obey the phase rule.

By a misunderstanding of Le Chatelier's data (1883), the calcium oxide and carbon dioxide system has been supposed to throw light on the hæmoglobin question. But, *at a given temperature*, the calcium is present either entirely in the form of calcium oxide or calcium carbonate, according to the tension of carbon dioxide. At tensions below a certain value, different for each temperature, we have complete decomposition; at all tensions above this value, the whole exists as calcium carbonate, and there are no intermediate stages. At first sight, again, a solution of sodium bicarbonate in water seems more like the one we seek. At tensions of carbon dioxide between 0 and about 3 mm. of mercury, there is a series of

intermediate stages in which there are progressively increasing concentrations of the bicarbonate and decreasing concentrations of carbonate. But the explanation of this fact lies in the electrolytic decomposition of the salt. The presence of more HCO_3 ions results in a rounding off of the corner of the curve owing to reduced ionization of the salt. Again, there are some dyes which may exist in a reduced form, capable of taking up oxygen when exposed to the air. Experiments made by W. A. Osborne (not yet published) were unable to discover any one of these which was not either completely reduced or completely oxidized, as the phase rule would predict. All search has hitherto failed to find any chemical system similar to that of oxygen and hæmoglobin.

It will probably occur to the reader that the adsorption of gases by indifferent solids, such as charcoal, is, at a given temperature, in proportion to the tension of the gas. In fact, it was suggested by Wolfgang Ostwald (1908) that the taking up of gases by hæmoglobin is a case of adsorption. But we are met by nearly as many difficulties in this view as in that of chemical combination. The taking up of gases by charcoal follows the usual parabolic law, whereas that of oxygen by hæmoglobin in solution in distilled water follows the rectangular hyperbola of a unimolecular reaction. On the other hand, the curve given by the latter system in the presence of electrolytes, acids or salts, requires a value greater than unity to be given to the exponent of the equation for the reaction velocity, in some cases above 3, an exceptional value for the order of an equation for velocity of reaction. The curve approximates more to that for adsorption.

The fact that there is a saturation point, beyond which increase of oxygen tension gives no measurable increase in the amount taken up by hæmoglobin, is not in itself, of course, inconsistent with adsorption. But, again, it is a remarkable fact that the accurate determinations of Peters (1912) have shown that the amount of oxygen taken up in saturation is exactly that required to combine with the iron in the hæmoglobin molecule to form FeO_2; in other words, one molecule of hæmoglobin combines with one molecule of oxygen. It is natural to associate the iron with the taking up of oxygen, but there is no other compound of iron having the properties of hæmoglobin. Even the hæmatin, which is combined with a protein to form hæmoglobin, behaves in a way similar to the dyes mentioned above. A further difficulty is the fact that hæmoglobin takes up carbon dioxide, carbon monoxide and nitric oxide in a similar dissociable way to that in which oxygen is taken up, although in different amounts. Just as in adsorption, one of these gases drives out more or less completely another one. The adsorption spectra of the CO and NO compounds is very like that of oxy-hæmoglobin, although there is a difference between all of them and reduced hæmoglobin. In any case it must be a remarkable chemical substance to combine with such dissimilar substances. According to Buckmaster and Gardner (1910–1911), chloroform is also taken up by hæmoglobin, driving off part of the oxygen.

In this connection, the relative adsorbing capacity of charcoal for various gases and vapours, the displacement of a weakly adsorbed

gas by a more strongly adsorbed one and the " spoiling " of the surface by adsorbed impurities are problems of much interest and importance, not only in relation to the hæmoglobin question, but especially in relation to the properties of the material used for the box respirator for protection against poison gases. It will be remembered that Faraday showed how readily the activity of platinum was stopped by the deposition of impurities from the air of the laboratory and that they could be driven off by heat. Investigations on these lines, from certain aspects, have been carried out by the Anti-gas Department, but are not yet made public. Bancroft (1918) states that carbon monoxide decreases the action of platinum in causing combination between oxygen and hydrogen gases and that it is tenaciously retained by the surface.

When hæmoglobin " combines " with oxygen, heat is evolved, but the results obtained by different investigators vary so much that it is scarcely worth while quoting them. It is well known that adsorption of gases by charcoal is attended by evolution of heat, so that the fact does not exclude the hypothesis of adsorption by hæmoglobin. The condensation of a gas on the surface is equivalent to a reduction of volume by compression.

The behaviour of the oxy-hæmoglobin system to a rise of temperature is similar to that of an adsorption process. That is, the *rate* at which oxygen is taken up is increased, but the *amount* held in equilibrium is less than at a lower temperature.

There are thus difficulties involved in both views, that of chemical combination and that of adsorption. It may be that the explanation may be found in a double process, such that the amount of oxygen taken up at a given tension is determined by the amount adsorbed, and that the adsorption is followed by chemical combination. But it is by no means easy to understand the mechanism of such a process. At any rate, it is obvious that hæmoglobin is a very extraordinary chemical compound and that its relation to gases is far from being explained up to the present.

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THE ADMINISTRATION OF COLLOIDS IN DISEASE.

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The general trend of pathological research has shown that the human body possesses in a varying degree the power of protecting itself against diseases of a parasitic nature, and that the protective medium is chiefly found in the blood.

Parasites such as bacteria do not usually kill by their mere presence in the body, but because they produce poisons. The body in normal health reacts to these poisons producing an anti-toxin which either neutralises the poison or kills the parasites producing it. If, however, the body is unable to produce such anti-toxins in sufficient quantities it is necessary to supply them artificially.

Some diseases appear to be due to an alteration of the blood owing to the presence in it of an excess of some substance such as uric acid or to a deficiency of certain inorganic elements which appear to be necessary to effect complete metabolism.

Modern methods of treatment therefore tend to follow four lines of development:

(*a*) The use of purer forms of well-known remedies, such as quinine hydrobromide instead of a decoction of cinchona bark, or morphia instead of tincture of opium.

(*b*) The administration of the elements or salts which are temporarily deficient.

(*c*) The use of substances having a selective action on the parasites which have invaded the body (see later).

(*d*) The increased production in the serum of the patient of the protective or curative substances which would be produced in insufficient quantities by the body under normal conditions. For instance, a healthy nurse will not usually be attacked by the disease from which the patient suffers, as the body will produce sufficient protective substances. In a less healthy person insufficient protective material is produced unless the corresponding stimulus is given to ensure its formation.

The medicines in the first group are improved by investigating their chemical composition, isolating the pure alkaloid or other essential ingredient from the mixture ordinarily used or by preparing the drug synthetically. There are obvious limitations to this procedure, and there are strong reasons for supposing that only a portion of even the purest drugs are required by the organism. In other words, the first group tends increasingly to be absorbed by one of the others.

Remedies of the (*b*) group are relatively simple when once the most suitable form of administration has been learned. The chief difficulty of the investigator is to obtain them in a form in which they will react in the desired manner so as to form the correct chemical compound required by the tissues. E. Dubard, for instance, has obtained evidence that a deficiency of magnesia in the system facilitates the development of cancer, but he has been unable to retain the magnesia in the system unless it is administered in such

large doses (12 grammes daily) that the excess of it produces undesirable effects. Such a difficulty clearly shows that the medicine has been administered in an unsuitable form.

The chief advances in chemistry during the past thirty years have been due to the development of the theory that chemical reactions occur between the ions or ultimate portions into which compounds are decomposable. Hence, an element in which the body is deficient must eventually be reduced either to its ionic state or to a form of combination which is equivalent to it.

In many cases, substances in a colloidal state react with an activity which is otherwise unobtainable. This may, in part, be due to the fact that when complete dissociation into ions is required the solutions must usually be exceedingly dilute, whereas colloidal solutions may be much stronger. Hence, the use of colloids has proved invaluable as a means of making good the deficiency in certain elements from which some tissues suffer.

Diseases which require selective remedies (group *c*) are chiefly those due to parasites, including the bacilli, micrococci, and other "germs" which produce certain poisons or toxins.

A substance which exerts either a toxic or a healing action on the body usually shows a greater affinity for one set of tissues than for others. Some substances have a greater action on bacteria and other parasites than on the host, and *vice versâ*. In other words, their action is selective, and an ideal medicine would be one which is so powerfully selective as to be absolutely fatal to the parasites it is desired to destroy and yet wholly harmless to the patient.

Ehrlich showed that a toxin is capable of producing disease only in those persons whose body-cells contain substances capable of entering into chemical combination with the particular toxin.

The anti-toxins and bacteriolysins appear to be equally definite in composition. Ehrlich found that an aniline dye, to which he gave the name of trypan red, is highly toxic with respect to trypanosomic parasites in blood but relatively harmless to the host.

According to Metchnikoff's popular theory of phagocytosis, the wandering corpuscles or leucocytes in the blood attack the bacteria or other parasites, but this theory has receded in consequence of the discovery by G. F. Nuttall, who, when working in Flügge's laboratory in 1886, found that anthrax and other bacteria died rapidly in fresh blood serum without the interposition of the leucocytes, thus showing that the serum itself contained the (chemical) substances which brought about their destruction. This is to some extent incompatible with Ehrlich's endeavours to seek a substance which is parasito-tropic without being organo-tropic, because a drug injected into the blood stream—either directly or intramuscularly—does not usually exhibit any action until it has been taken up by the serum. Hence the organo-tropic (as distinct from the organo-toxic) properties of a drug are of great importance. So far, no substances have been found which are highly parasito-tropic and wholly devoid of organo-tropic properties, though many colloidal sols are so feebly organo-tropic as to be devoid of danger in any ordinary doses. In the case of elementary colloids such as mercury or iodine, any toxic symptoms and ill effects may be removed

by the administration of a colloid of the opposite electrical charge (a metal to relieve an excess of non-metal and *vice versa*). Whilst, as a rule, no coagulation occurs when colloidal solutions of the same electric sign are mixed, if a solution of the opposite sign is added coagulation occurs unless one of the colloids is in very large excess. Before the science of chemotherapy had advanced to its present stage, and even now as regards certain diseases, successful remedies were found by what is known as the serum treatment in which the requisite anti-toxins are prepared by cultivating suitable bacteria, etc., and using the products which they have formed. Investigations have also been made with a view to synthesising the anti-toxins (or those portions of them which are required for the purpose) in order to eliminate certain objectionable features of the serum treatment. Endeavours have also been made to simplify the materials used, by supplying the body with just those elements or groups from which it could most rapidly prepare the material which would stop the progress of the disease and facilitate a cure.

Still further investigations have shown that all the normal fluids and secretions of the organism are essentially colloidal in character, the toxins or bacterial poisons appear also to be in the colloidal state and to a large extent the reactions which create immunity to certain diseases are typical of those met with in ordinary chemical absorptions and precipitations. This at once suggests the importance of colloidal substances, both in the maintenance of health and in the cure of disease.

Graham,[1] to whom we owe the conception of the colloidal state, clearly saw the importance of colloids for living matter, when he wrote, "The colloidal is, in fact, the dynamic state of matter; crystalloidal being the static condition. The colloid possesses *energia*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place may the characteristic protraction of chemical organic changes be referred." These words are prophetic of what is now recognised with regard to the relation of colloidal and living matter, whether healthy or diseased, and, so far as is known at present, the physico-chemical conditions necessary for life can be accurately summarised in the statement that *all life-processes take place in a colloid system*,[2] only those structures being considered as living which are at all times in a colloidal state.

According to J. Beatty,[3] all enzyme action, whether of hydrolysis, synthesis, oxidation, or reduction, can ultimately be traced to the addition or removal of hydrogen or hydroxyl radicles in hydrolysis or synthesis, and to the replacement of H by OH or OH by H in oxidation and reduction respectively. In the presence of a catalyst the speed of reaction may be increased, or its sphere of action limited, the latter being controlled by the colloidal nature of enzymes, whereby reactions are brought about as the result of surface adsorption.

[1] Phil. Trans. 1861, 151. 184.
[2] Wolfgang Ostwald. "Colloid Chemistry," New York, 1917.
[3] "The Method of Enzyme Action," London, 1917.

Many animal organs behave exactly like gels when immersed in water and swell enormously. This swelling is affected by the presence of small proportions of acids, alkalies or salts in the water. Thus, in the case of gelatin, fibrin and egg-albumin, acid solutions of moderate concentration greatly increase the amount of swelling and the amount of water absorbed by the organic substance. This is due to the presence of free hydrogen ions. On the other hand, the addition of a suitable alkali or salt will reduce the swelling and restore the substance to its previous condition, by neutralising the excess of free hydrogen ions. If an excess of hydroxyl ions be added in the attempt to reduce the swelling, the gel may be peptised and "dispersed." A typical glaucomatous state may be induced in sheep's eyes *in vitro* by immersing them in very dilute hydrochloric acid. The normal condition may be restored by the addition of ferric chloride or other appropriate salts. Precisely the same phenomena are observable with living tissues, both in health and disease, and any desired colloidal condition may be obtained in the latter by appropriate colloidal treatment. Thus, the administration of salt has been successfully employed in the treatment of nephritis and œdema.[4] The extensive use of salines solutions in various stages of collapse has long been practised in all civilised countries, and its success is due to the action of these substances on the colloidal serum. Such salts prevent the swelling and coagulating effects of the acids formed in the diseased tissues, just as they decrease the effect of other acids, or effect the precipitation of certain colloids *in vitro*.

Inflammation is also a colloidal phenomenon, and is brought about by precisely similar conditions in the living subject, and in artificially prepared plates of non-living materials.[5] It is easy, for example, to produce "artificial flea bites" by pricking a piece of gelatin with a needle dipped in formic acid and then placing the gelatin in water.[6] The remedy—injecting into the swollen portion sufficient alkali to neutralise the acid—is as efficient as when this method is applied to a real bite. The complete comparison of these "bites" with the phenomena observed when a flea bites the human subject is, however, a very difficult matter.

The unknown substance which produces goitre[7] is most probably colloidal in nature. Hence, from one point of view, therapeutics is largely concerned with a study of the formation of colloids which are abnormal in the sense that they do not occur in the natural processes of a healthy body, but which—when regarded as colloids—are no more unusual than the coagulation of a highly dispersed sol or the peptization of a coarser gel. The chief difficulty in the way of experiment or treatment is that in one case conditions are severely restricted owing to the fact that the colloids form part of a living organism.

[4] M. H. Fischer, *Œdema and Nephritis*, New York, 1915.
[5] A. Oswald, *Zeitsch. f. exp. Pathol. u. Therapie*, **8**, 226, 1910; *Koll. Zeit.*, **9**, 251 (1911).
[6] M. H. Fischer, *Œdema and Nephritis*, New York, 1915, pp. 199, 602.
[7] E. Bircher, *Ergebnisse der Chirurge u. Orthopædie*, **5**, 133; *Zeits. f. exp. Pathol.*, **9**, etc.

Many of the recognised methods of treating disease are efforts made with a view to altering the colloidal state of some portion of the patient's body, such as the reduction of a swelling by the dehydration of an unduly hydrated gel or varying the amount of dispersion of the colloidal particles in another part of the system. Thus, it is now quite recognised that many of the most familiar medicines are crude preparations of a colloidal character in which the action of the essential ingredient has been largely obscured by the presence of adventitious substances, some of which possess undesirable or even toxic properties. The digestive disturbances caused by the administration of iron compounds, the headaches which accompany the administration of quinine, and the pain resulting from the use of silver compounds are well known examples of the interference of some subsidiary ingredient of an otherwise useful therapeutic agent.

Many attempts have been made to avoid these complications. In some instances, remarkable results have followed the use of extremely dilute (*i.e.*, fully ionised) solutions; other investigators have sought to eliminate the disturbing elements and to produce purer medicines, and others again have endeavoured to counteract the irritants by using two or more drugs in combination. Each of these methods has resulted in a certain amount of progress. For many years, however, the essentially colloidal character of the recognised remedies was overlooked, and the fact was not realised that before a drug can exert its full therapeutic action it must be converted into the colloidal state.

One of the earliest to appreciate the importance of using therapeutic agents in a colloidal state was the late Henry Crookes who, in 1911, after making protracted experiments, found a means of producing stable preparations of colloidal silver, copper, iron and mercury, which were not precipitated by saline solutions. To these he gave the name "Collosols." Since that time, stable preparations of colloidal solutions of sulphur, iodine and manganese as well as those of a much more complex character including some of the alkaloids cocaine, etc., have been used extensively by leading medical practitioners with wholly satisfactory results. The use of unstable colloidal sols has, on the contrary, been far from satisfactory and has led to serious misconceptions as to the value of remedies in the colloidal state.

Owing to their condition, stable colloidal sols behave in a manner quite different from other synthetic medicines. The latter—even when dissociated—contains two distinct groups of substances, one positive and the other negative. So far as is at present known, a diseased organism is deficient in either positive or negative ions, or it has an excess of one of these kinds of ion and is unable to get rid of it. The former case is much more common than the latter. The natural remedy is the presentation of further ions of such a character as to make good the deficiency or to remove the excess. If solutions of chemical compounds of a crystalline nature are administered they must first be dissociated and the requisite ions will then be available for use. The action of the ions which are opposite in character to those required by the body may be either disadvantageous or neutral,

but as their presence is accidental, if it could be avoided it would clearly be to the benefit of the patient.

By the use of certain colloidal preparations it is possible to attain this desideratum and to restore the organism to its normal state of ionisation in a relatively simple manner, without the complexities caused by the presence of unwanted ions. Thus, an anæmic patient will be assisted by the administration of iron in a form in which the amount of hæmoglobin in the system can be increased, but the administration of excessive doses of an unsuitable compound of iron will be useless for this purpose and will be detrimental in other ways, such as disturbing the digestive functions. The introduction of a soluble salt of iron into the serum will not necessarily increase the amount of hæmoglobin, though the organism has a remarkable power of utilising apparently unsuitable materials. Briefly, it does this by first extracting some of the required agent (as when the gastric juices dissolve the ferrous carbonate in a Blaud's pill), then, as the solution is usually very dilute, the agent becomes dissociated and the required ions are utilised by the organism and unnecessary ones being eventually discharged. It is obvious, however, that if a therapeutic agent is presented in the form in which it is required—which in the case of many substances is in the state of a colloidal sol—much unnecessary waste of vital energy is avoided, the specific action is more direct and efficient, a loss of time which must occur before the body has effected the preliminary conversion is saved, and troublesome, or even dangerous, side reactions are avoided.

The difference between the action of many medicines and the corresponding colloidal sols is remarkable. Thus, a 2 per cent. solution of iodine in either alcohol or potassium iodide stains the skin badly, and when administered internally is very liable to give rise to iodism. This is avoided by using a colloidal solution of iodine of the same or even greater concentration.

It is, of course, of the utmost importance that colloidal medicines shall be in a suitable state. Colloidal gels are of value in certain cases, but far more important are the colloidal sols. The latter are difficult to prepare in a stable form, and unless they are resistant to the action of the electrolytes normally present in serum they are useless for therapeutic purposes, as they would be precipitated before they could effect the desired purpose. Fortunately, it is easy to test the stability of a colloidal sol by examining it under the ultra-microscope after mixing it with various solutions in respect of which its stability may be questioned.

Colloidal medicines which have not been prepared in a proper manner also decompose on long standing. They then show a precipitate, the amount of which increases as the decomposition continues. Properly-prepared, stabilised colloidal sols are quite permanent. The writer has kept collosol iodine and collosol silver for two years at a temperature of 70°F., and on examining them under the ultra-microscope at the end of this period could observe no difference in activity as compared with that of freshly prepared collosol. On the other hand, a colloidal silver prepared by Bredig's method was feeble after four weeks and inert after seven weeks when

kept under the same conditions. The existence of the agent in a suitable and permanent colloidal state is, therefore, essential.

In a general sense, sols may be stabilised by preparing them in the presence of an emulsoid, such as gelatin, which appears to surround the particles of sol and renders them less sensitive to salt solutions. Such protected sols may be evaporated to dryness and the residue—which is usually in the form of dark scales—can be brought back into a state of colloidal sols by the addition of water. If such " dried hydrosols " have been prepared from exceptionally pure materials and with unusual care and skill, they form, when dropped into water, colloidal solutions in which the sol has the same properties as those previous to evaporation. The present writer has found, however, that the commercial " dried hydrosols " which he has examined (which are sold under a variety of fancy names) have seldom been prepared with sufficient skill, and therefore do not yield " solutions " of the same power and therapeutic value as can be obtained without evaporation; the advantage of portability gained by the production of the dried product is more than counterbalanced by the uncertainty as to the strength and activity of the sols produced by adding tap water to them in vessels which have not been specially prepared for the purpose, and by their instability in the presence of salts. For these reasons, he does not favour the use of the dried preparations, except in cases where it is impossible to use those which have not been dried. Moreover, the stability of colloidal sols depends more on the mode of preparation than on the presence of a stabilising agent. Hence, excellent therapeutic results have been obtained with some colloids to which no protective has been added.

It was realised about ten years ago that colloidal sols of certain metals inhibit the growth of all known bacteria, and it has since been found that they are harmless to the tissues. For this reason the use of colloidal sols has an enormous field of usefulness. They can be administered orally or injected in any desired quantities without any risk of toxication or undue shock to the system.

The normal effects of colloidal sols on the blood stream is shown by the following experiment[8]:—

"A rabbit, weighing 1 kilo., was injected with 2 c.c. of collosol hydrargyrum in the auricular vein on the 14th of the month; on the 16th of the same month 3 c.c. more were injected. There was no local reaction, no bad symptoms; the rabbit did not go off its food. On the 16th it was killed by the usual method, viz., chloroform. The arterial system of head and neck were perfused with normal saline solution (the eyeballs were very tense). The cerebro-spinal fluid was extracted under somewhat increased pressure. A post-mortem examination of the rabbit showed no change. A sample of the urine was taken, and also a slice of the cerebral cortex, which was emulsified and allowed to settle.

" These three fluids were examined under the ultra-microscope, and the observations made were as follows:—

" The cerebro-spinal fluid showed a distinct cone, with many colloidal particles having a strong Brownian movement.

[8] H. Crookes, "Recent Work on Metallic Colloids," *Journal of Chemical Technology*, July, 1915.

"The supernatant fluid from emulsion of the brain section showed the cone distinctly with occasional colloidal particles.

"The sediment stirred up with sterile water showed many coarse particles and a large number of colloidal particles, many having a green colour with strong Brownian movement.

"The urine showed a strong cone of light, no coarse particles, but a very large number of colloidal particles with a strong Brownian movement.

"These results prove that when 'collosols' are given by intravenous injections they permeate throughout the entire system, and that the unutilised or excess portion passes off with the urine."

The toxicity of colloidal substances depends largely on the manner in which they have been prepared and on the presence of associated substances. If sufficiently pure and suitably stabilised, many of them appear to be wholly non-toxic; but impure or unstable preparations are toxic in proportion to their instability or to the adventitious substances present. Colloids such as mercury and arsenic, which are not normal constituents of the body cells, are liable to be toxic in nerve tissue[9]; but if wholly in the sol state and properly sterilised, their toxic power is insignificant, and they can be injected intravenously or intra-muscularly with impunity, and with extraordinarily good results.

The first effect of injecting a suitable sol into the serum is to break up any large protein particles into small ones, thereby increasing their surface area and activity. After this, the various colloidal materials react, forming the substances required to effect the necessary readjustment of the serum and to restore it and the tissues to a state of normality. When parasites are present, the protein particles in the serum appear to attack them by some form of surface action, the nature of which is not clearly understood though it appears to be analogous to the action of staining by aniline dyes. Hence, the importance of these protein particles being as small as possible and of the metallic colloids in stimulating and accelerating their destructive action.

Expressed in more physico-chemical terms, the blood stream of man, like the contents of the cells of all living organisms, is a peculiarly sensitive fluid. A slight alteration in the fluids which surround it (in adjacent tissues) and even in its own contents brings about changes which are so great as to produce illness or even death.

Lord Lister[10] showed that the introduction of septic material into the blood gives rise to the development of large cells or flocculent matter which partially decompose with the formation of a thick yellow fluid of a highly toxic character.

Blood serum is, in fact, a typical emulsoid colloid though it is characterised by so high a degree of dispersion that it shows the Tyndall cone only feebly.[11] Equally significant is Hardy's observation[12] that protein is electro-negative in an alkaline solution and electropositive in an acid one. The blood serum in normal health is

[9] J. E. R. McDonagh, *Brit. Med. Journal*, May 19, 1917, p. 648.
[10] Collected Papers (1909), ii. 541.
[11] Winterstein, *Hand. C. d. vergl. Physiologie I*, 415.
[12] *J. Physiol.*, 1899, 24, 288.

alkaline, and has a prevailing hydroxyl concentration. In many diseases this alkalinity is reduced with consequent toxic symptoms. To restore normality it is therefore necessary to reduce the concentration of the hydrogen ions or to increas that of the hydroxyl ions. The choice between these must depend on other circumstances, and especially on the relation of the relative concentrations of the serum of the patient in disease and in health.

An interesting instance of the importance of a knowledge of the properties of colloids in the treatment of disease occurs in anæmia. In the simplest case this disease is due to a deficiency of iron in the hæmoglobin in the blood stream. Hæmoglobin is electro-positive, and to increase its amount without disturbing the general characteristics of the serum, any iron compound administered must also be electro-positive when it enters the blood stream. For this reason iron carbonate and hydroxide are useful whilst such compounds as ferric chloride which are electro-negative and act as coagulants should be avoided. The objection to iron carbonate and hydroxide lies in the fact that they are usually converted into ferric chloride or analogous compounds by the gastric juices and so largely fail to reach their destination in a useful form.

Colloidal iron, on the contrary, not being affected by these juices, is able to enter the blood stream in a satisfactory and therapeutically active form.

The retention of an unnecessary amount of any substance in the blood stream or tissues tends to induce toxicity. The extremely minute size of the particles in the colloidal sols is such that they pass readily through the tissues and the chances of their being improperly stored in the system are correspondingly[13] minimised. In view of the foregoing facts it is not surprising that colloids are coming more and more to the front in pharmacology[14], particularly those which approach the state of true solutions. A good example is seen in Fischer's work on œdema[15] in which he has shown that œdema results from imbibition of water by certain colloids.

The choice of a colloidal sol suitable for a particular pathological condition must naturally depend on the cause of that condition. This can only be ascertained by trial, though certain broad conclusions may be reached with respect to the chemical behaviour of different substances. In the colloidal state, however, many substances react entirely differently from what may be regarded as their normal behaviour. Thus, colloidal sulphur sometimes acts indirectly as an oxidising agent and both metals and non-metals act in a manner which cannot be predicted on general chemical grounds.

The use of colloidal copper injected intravenously can aggravate boils if administered in large doses. In smaller quantities and injected intramuscularly, it has the opposite effect, but is far inferior to colloidal manganese for this purpose. Indeed, colloidal manganese

[13] Sir J. J. Thomson (Royal Institution, March 23rd, 1912) stated that one drop of a metallic collosol contains more than 1,000,000,000,000 particles of metal which cannot be detected by ordinary methods and pass readily through the pores of a filter.

[14] Porges, *Koll. Zeit*, 5, 301 (1909).

[15] *Das Odem*; *Eine Expt. u. theor. Untersuchg. d. Physiologie und Pathologie* (1910).

differs from all other remedies in that when it is used for the treatment of boils it is only very occasionally that fresh boils make their appearance during the treatment and these quickly subside without further trouble. Colloidal manganese appears to be particularly indicated in the treatment of staphylococcic infections.

Turning now to the specific effects of various collodial substances, it should be noted that the following are all in the sol state and that they must (for reasons previously indicated) have been suitably stabilised.

All these colloidal sols are thin fluids containing the colloid in so finely suspended a condition that it passes readily through a filter.

Colloidal silver containing 0·05 per cent. of the metal in a colloidal form and not as a salt, is a clear, cherry-red liquid which has been used by C. E. A. McLeod with marked success in the following cases:—

By local application on septic and follicular tonsilitis; Vincent's angina; phlyctenular conjunctivitis; gonorrhœal conjunctivitis; spring catarrh; impetigo contagiosus, acne of face and body; septic ulcers of legs; ringworm on body; tinea versicolor; soft sores; suppurative appendicitis after operation (the wounds cleaned rapidly); pustular eczema of scalp and pubes; chronic eczema of meatus of ear with recurrent boils and also chronic eczema of anterior nares; offensive discharge in case of chronic suppuration in otitis media; bromidrosis of feet and axillæ; blind boils on neck. By injection: gonorrhœa and chronic cystitis (local), boils, epididymitis. It has also been injected intravenously in general blood infections, pneumonia, bronchitis and phthisis in doses of 15–45 minims, with marked success.

Sir James Cantlie has found it particularly effective in cases of sprue, dysentery, and intestinal troubles. The dose can be increased from one to two or more drachms twice or thrice daily without danger.

A. Legge Roe regards stable colloidal silver as a most useful preparation[16] in ophthalmic practice and particularly in cases of gonorrhœal ophthalmia, purulent ophthalmia of infants, infected ulcers of the cornea and hypopyon ulcer (tapping of the interior chamber and cautery and other operative procedures being now rarely required, whilst if perforation does occur it is smaller and more manageable), interstitial keratitis, blepharitis, dacryocystitis and burns and other wounds of the cornea.

T. H. Sanderson-Wells used it successfully intravenously in a case of[17] puerperal septicæmia, without any irritation of the kidneys and with no pigmentation of the skin. This physician has found that a series of intravenous injections each of collosol argentum every 48 hours produces no untoward effects and that recovery is rapid.

Sir Malcolm Morris has found that colloidal silver is free from the drawbacks of other preparations of silver, viz., the pain caused

[16] *Brit. Med. Journ.*, Jan. 16, 1915.
[17] *Lancet*, Feb. 16, 1918.

and the discoloration of the skin[18]; instead of producing irritation, it has, indeed, a distinctly soothing effect. It rapidly subdues inflammation and promotes the healing of lesions. He has had remarkable results in enlarged prostate with irritation of the bladder, in pruritis ani and perineal eczema, and in hæmorrhoids. It can be used in the form of suppositories while a solution is applied to the irritated skin. In bromidrosis in the axillæ and feet it quickly gives relief. It causes a rapid disappearance of warts. Being non-toxic, it can be given internally in urticaria and other forms of dermatitis which are suggestive of toxæmia. In such cases it is quickly beneficial .

In ophthalmology, colloid silver has now largely replaced silver nitrate as its use is free from pain and its action more direct.

J. Mark Howell has found colloidal silver beneficial for permanently[19] restoring the potency of the Eustachian tubes and for reducing nasopharyngeal catarrh.

Colloidal silver has also been used successfully in septic conditions of the mouth (including pyorrhœa alveolaris—Rigg's disease), throat (including tonsilitis and quinsies), ear (including Meniere's symptoms and closure to Valsava's inflation) and in generalized septicæmia, leucorrhœa, cystitis, whooping cough, and shingles. Tests made at King's College show that colloidal silver has an inhibitive effect on bacteria equivalent to mercuric chloride, but is non-toxic, non-irritant and harmless to the host.[19A]

A preparation of colloidal silver which is opaque to X-rays has proved invaluable in certain diagnoses.

Colloidal mercury. The curiously different action of mercury salts according as they are given in small or large doses and in a readily or difficult soluble form have long puzzled pharmacologists. It has been readily understood that their action is antiseptic and bactericidal, but according to some of the best known authorities, the chief action of mercury is to increase the natural resistance of the body to disease. The chief disadvantage of the less soluble mercury salts, such as calomel, is their delayed and irregular absorption, with subsequent undesirable results. The soluble mercury salts, on the contrary, are dangerous on account of their high toxicity. With colloidal mercury, the diffusion is extremely rapid and chemical affinity low. Hence, the toxicity of colloidal mercury (1—2,000) is so low that doses of two teaspoonfuls may be taken twice daily or intravenous injections of 30 c.c. may be given with impunity.

Colloidal mercury has cured persistently relapsing malaria in a few days.[20]

Some of the colloidal preparations of mercury on the market are not suitable for oral administration, but must be injected intramuscularly. Colloidal mercury is chiefly used in syphilis.

Colloidal iron, according to Lyn Dimond, killed within six minutes, such organisms as bacillus typhosus, bacillus coli communis and various pyogenic cocci. The solutions seem to have a definite

[18] *Brit. Med. Journ.*, May 12, 1917.
[19] *Brit. Med. Journ.*, Dec. 15, 1917.
[19a] *Lancet* (1914), p.
[20] G. Cremonese, *Garr. d. osp.* (1918) **39**, 427.

elective bactericidal action upon catarrh-causing organisms as pneumococcus and various strains of the micrococcus catarrhalis. Rapid relief followed the topical application of the solution in cases of catarrh of the nose, larynx or pharynx. Colloidal iron is also used, by subcutaneous intramuscular and intravenous injection, in cases of extreme chlorosis, anæmia, erysipelas and cellulitis.

Iron is almost the only metal found in the animal organism which is also obtainable in a colloidal state in the presence of water. The significance of this fact has not yet been sufficiently recognised. In the serum, the iron is probably present as a protein compound the precise constitution of which has not yet been determined. The total iron content of the normal body does not exceed 37 grains, and although several organic compounds of iron have been recommended they are by no means satisfactory being either too feeble in action or too readily decomposed *in corpore* and so rendered useless. Inorganic compounds of iron are held by many practitioners to be the most efficient in what they consider to be the only true test of the value of an iron preparation, *i.e.*, an increase of hæmoglobin in the blood. The administration of iron in the form of a colloidal sol appears to be a simple means of increasing the amount of the protein compound in the serum, as this form of iron, when administered orally, is rapidly diffused in the stomach and yet it is not absorbed in individual positions. It is found that the amino-acids formed during the process of a digestion are readily able to absorb into their complex molecule a large proportion of the iron administered in the colloidal form and from it to effect the synthesis of hæmoglobin. This is in marked contrast to the behaviour of the carbonate, hydroxide and chloride of iron usually administered.

Colloidal antimony has been used in conjunction with manganese with extremely good results in gonococcic infections. In India it has given very satisfactory results in Kala-azar, its administration in this disease being accompanied with less risk than that of arsenic.

Colloidal manganese has been used with remarkable and surprising results in the treatment of coccogenic skin disease, including deep abscesses, boils and deep-seated impetigo. In superficial impetigo, chronic seborrhœic eczema and acute folliculitis it is of little value when used alone, but gives excellent results when employed in conjunction with intramine. The rapidity of its action[21] combined with the saving of dressings render the use of this form of manganese very attractive in deep-seated coccogenic lesions. It is usually injected intra-muscularly in amounts of 3 c.c. every few days. In most cases one injection is sufficient.

J. E. R. McDonagh[22] has also used intravenous injections of 33 c.c. of colloidal manganese with excellent results in the treatment of poisoning by mustard gas (dichlorethyl sulphide) and other cases of sulphur poisoning.

Colloidal copper is useful in the treatment of boils, though it is inferior to manganese for this purpose. In malignant diseases, the intra-muscular injection of copper has proved highly beneficial, the

[21] J. E. R. McDonagh, *Medical Press and Circular*, Dec. 5, 1917; Sir Malcolm Morris, *Brit. Med. Journ.*, Apl. 20, 1918.

[22] *Medical World* (1918), p. 137.

metal having been shown to be present in the growth within 24 hours after injection. Copper is known to have a strong inhibitive action on low forms of life. Herschel, de Gres and others have stated that colloidal copper exerts an inhibiting action on all cell metabolism. In this connexion it is important to note that cases of cancer in which copper can be shown to be present in the growth are certainly the ones which are the most amenable to treatment. The difficulty lies in causing the copper to penetrate the periphery of the cancer. Pessaries of colloidal copper in glyco-gelatin have proved serviceable for uterine fibroids.

Colloidal arsenic (0·2%) in doses of 2 c.c. has an extraordinary effect in pernicious anæmia and herpes deformans. The simultaneous presence of a liquid or colloidal protein appears to be essential to the proper reaction of arsenic. Thus, salvarsan *per se* has no action on the spirochæta pallida, which can move readily for some hours in a solution of salvarsan. Yet the introduction of a little serum or digested protein will cause their immediate death. The elimination of arsenic from the system is usually a matter of difficulty, but in the colloidal form its low toxicity combined with the small dosage reduce the risk of its retention to a minimum.

Colloid palladium oxide has been applied successfully in the treatment of obesity by injecting it hypodermically into the fatty areas.[23]

Colloidal palladium sol has proved of value in gonorrhea.

Colloidal nickel has been used in meningitis.

Iodine was discovered in 1811. In the form of an alcoholic solution it soon became popular, but was afterwards neglected for many years. More recently, it has been brought prominently forward and at the present time[24] it is almost the only chemical antiseptic, except alcohol, employed by a large number of British surgeons.

Colloidal iodine may be obtained in three forms: (i.) aqueous, (ii.) oil and (iii.) paste or ointment. The aqueous colloid (1 in 500) contains the element in its most active form, and is suitable for administration in all cases in which iodine or an iodide is indicated. Its action is more gradual than that of a solution of iodine, but more certain than that of iodides, and there is complete avoidance of "iodism" and nausea. The whole of the colloidal iodine is absorbed, whereas 85 per cent. or more of the ordinary iodides administered are excreted within 24 hours.

When injected intravenously, the action of colloidal iodine is more rapid, and as much as 300 c.c. has been injected with impunity in cases of pyæmia, also to effect a softening of fibrous tissue, thus showing its abolute nontoxicity. *Per se* colloidal iodine is only slightly parasitotropic and bacteriotropic, but microorganisms are very greatly influenced by its action and the effect of a subsequently administered remedy is greatly increased.

[23] M. Kauffman, Münch. Mediz. Wochenschr., 525, 1913.
[24] Sir R. J. Godlee, Lord Lister (1917), 158.

Colloidal iodine is also indicated in syphilis by prior injection, and also by internal administration, and in cancer by intravenous injection.

In rheumatism, a piece of flannel soaked in colloidal iodine, attached to the positive pole of a battery and applied as near as possible to the affected area has been successful. It has also been used beneficially as a spray in bronchial and nasal catarrh and internally in recovery from alcoholism.

Colloidal iodine oil (3 per cent.) is very useful for eczema and other forms of affections and abnormal conditions of the skin. On application, the iodine particles penetrate the pores of the skin without staining the epidermis, the latter being kept supple and soft by the hydrocarbon oil in which the colloidal iodine is exhibited and stabilised. Thus, the staining and hardening effects of alcoholic and other solutions of iodine are avoided.

In some cases[25] of bad chilblains, colloidal iodine oil was rubbed in four times a day; every trace of the condition disappeared in four days. Equally valuable is this colloid in severe cases of trench feet with ulceration and in the many cases of Charcot's bedsores which are so troublesome a complication of spinal injuries in military hospitals. In the earlier inflammatory stages of lupus erythematosus, before atrophy has supervened, it is far more suitable than the ordinary form of the drug because of the absence of irritation. Similarly, it is to be preferred for internal administration in the later stage of syphilis, because there need be no fear of iodism. Parasitic affections, again, show a striking amenability to this remedy. In a case of dhobie's itch (in which the disease had spread from the groin and invaded the trunk, legs and arms) under the quite painless application of colloidal iodine oil, the extensive lesions all cleared up in three weeks; with ordinary remedies the case would undoubtedly have been more protracted, and the treatment would inevitably have put the patient to a good deal of pain.

Colloidal sulphur (1 per cent.) has proved invaluable in cases where there is a deficiency of this element in the system. The value of sulphur has long been known, but the forms in which it is usually administered are crude. It has been necessary to employ excessively large doses of an insoluble form of sulphur or to administer "Harrogate water" or some equivalent and unpleasant preparation of hydrogen sulphide. There is little doubt that an insufficient amount of available sulphur in the system impairs the action of the liver, with consequent production of intestinal poisoning (constipation, headache, arthritis, etc.).

Colloidal sulphur is extremely active, readily combines with protein and is entirely absorbed in the stomach. The products of this combination are rapidly taken into circulation and those parts of the organism for which sulphur is necessary are thus supplied. Ordinary sulphur is not absorbed in the stomach at all, and passes practically unchanged into the intestines.

In many cases of rheumatism and neuritis and even in "arthritis deformans" relief has been rapidly obtained by its internal adminis-

[25] Sir Malcolm Morris, *Brit. Med. Journ.*, May 12, 1917.

tration. In acute rheumatism, the intravenous injection of colloidal sulphur has proved beneficial. Colloidal sulphur has also been found to increase the tolerance to mercury in syphilis when administered orally, and has given relief in some cases of cancer when injected subcutaneously.

Colloidal sulphur baths have been of service in rheumatic conditions and skin affections. The colloidal sulphur content in the bath is far greater than that of natural sulphur water, and as the bath contains no impurities or free sulphuretted hydrogen it is free from the many objections associated with the use of natural sulphur waters.

Sir Malcolm Morris has found that among the affections in which colloidal[26] sulphur is beneficial are various forms of acne (including acne rosacea and seborrhœa), generalised dermatitis, acute psoriasis and painful fibrositis, whether of connective tissue, of muscle, or of joints. Baths medicated with this colloid are, in his experience, at once soothing and quickly curative.

Colloidal alumina (gel)[27] has shown excellent astringent effects in various kinds of diarrhœa and is less toxic than the bismuth compounds usually administered in such cases.

Colloidal quinine (sol) appears to be free from the chief disadvantages of quinine salts, particularly in malaria. The fact that it is not so readily lost in the excretions is important as Hartmann and Zila[28] have found that less than one-third of the quinine salts ordinarily administered are retained by the body and that the amount found in the blood after oral administration did not exceed 3 per cent. of the dose taken. Further investigations are now being made on this colloid.

Production of Colloidal Remedies.

The production of colloidal solutions which are sufficiently stable to be used in medicine is largely a secret, few of the processes having been protected by Letters Patent. No single method either of peptisation or stabilisation is suitable for all the various sols required, and as prolonged and costly investigations are required before a really stable sol of high therapeutic value can be offered to the medical profession it is only natural that the manufacturers should keep the information to themselves. The general methods by which colloidal sols can be produced and rendered more or less stable are well known, and as a still larger number of substances is reduced to this state the number of methods used in their production will also increase. Of the methods which have been disclosed, the following are the most important, but it should be observed that none of these Patent Specifications have been taken out by the manufacturers of commercial available colloids used in medicine in this country and that they do not describe the methods used in producing the highly stable colloids which have yielded the results mentioned in the present report:—

No. 12,037/1911. F. Wrledter, Preparation of sols.

No. 1219/1912. A. Dering, Preparation of Colloidal Mercury

[26] *Ibid.*

[27] Eng. Pat. 104, 609.

[28] *Arch. f. exper. Path. u. Pharmakol.* 1918, **83**, 221.

No. 11,771/1912. E. Podszus, Preparation of sols.
No. 14,235/1912. B. Schwerin, Preparation of sols.
No. 29,049/1912. Ges. f. Elektro-Osmose, Preparation of sols.
No. 7238/1913. Aktiebol: Kolloid Preparation of Colloidal Sulphur.
No. 9237/1914. Ges. f. Elektro-Osmose, Preparation of Colloidal Silica.
No. 9261/1914. Ges. f. Elektro-Osmose, Preparation of Metal sols with silica.
No. 15,267/1914. Ges. f. Electro-Osmose, Preparation of Metal sols.
No. 15,127/1915. Soc. Chem. Ind. Basle, Preparation of Colloidal Copper.
No. 104,609 (1917). Monneron & Guye, Preparation of Colloidal Alumina gel.

Colloids and Synthetic Compounds.

There is no necessary incompatibility between colloidal sols and synthetic compounds which are not regarded as being in the colloidal state. Each of these groups of remedies has its own sphere of usefulness, and some of the synthetic drugs are more colloidal than is generally supposed (see section on Dyes in the 1917 B. A. Report on Colloids). In view, however, of the large amount of work which has been done by Ehrlich and others in the preparation of synthetic compounds of arsenic and other metalloids it appears desirable to draw attention to the following facts:—

The action of synthetic compounds is usually due to their high molecular weight and often to the presence of ortho-amino groups. In some cases, a metal or metalloid is separated in colloidal sol form in the blood, the remainder of the drug merely serving as a vehicle. In others, the whole compound acts as a reducing or oxidizing agent. It may or may not be a coincidence that the most effective therapeutic reducing agents contain a metalloid (such as sulphur or iodine) whilst the most effective oxidising agents contain a metal.

In this connexion it is particularly interesting to compare the almost non-toxic colloidal metals and metalloids with that of the well known salvarsans and their compounds containing phosphorus (galyl), platinum, gold, copper or silver. According to Kolle[29] the following doses are toxic to syphilitic rabbits; smaller doses are toxic to the human subject:—

	Toxic Dose grms.	*Tolerated Dose grms.*
Salvarsan	0·125	0·1
Neo-Salvarsan...	0·25—0·3	0·2
Hexamino-Salvarsan	—	0·15
Galyl	0·125	0·1
Bismethyl-Standard	0·28	0·22
Dichlorarsalyte	0 25	0·2
Dibromarsalyte ...	0·36	0·3 (?)
Diiodarsalyte	—	—
Copper Salvarsan K_3	0·04	0·035
Platinum Salvarsan	0·07	0·05
Gold Salvarsan	0·03	0·02
Silver Salvarsan	0·3	0·125

[29] Deutsche Med.-Wochenschr. 1918, **44**, 11, 1., 11727.

It is well known that most of these salvarsan compounds deteriorate and become more toxic on exposure to air. Thus within an hour the toxicity of neo-salvarsan increases 3 to 6 fold, the arsalytes within 24 hours increase 2½ times in toxicity, and the same applies to the metallic salvarsan compounds. Colloidal metal sols do not become toxic, even on prolonged exposure.

Hexamino-salvarsan in the moderate dose of 0·4 grm. has produced grave symptoms and even fatal results which led to its discontinuance. Gold and platinum salvarsan possess too great a toxicity for therapeutic use in man. Silver salvarsan, on the contrary, is 2 to 3 times as potent as old salvarsan and it is by far the most active form of salvarsan for destroying the spirochætes in rabbit syphilis and in curing the lesions. It has likewise been used with excellent results in man in doses of 0·2 to 0·4 grm. Kolle does not state the exact chemical constitution of this substance, but it is highly probable that much of the silver is in a colloidal state, especially as he found that colloidal silver (collargol) alone in doses of 0·03 grms. per kilo caused the rapid disappearance of spirochætes in the rabbit.

Colloids and Physiological Extracts.

The remarkable results which have followed the administration of certain physiological extracts (thyroid, pituitary, etc.) appear to be largely due to the presence, in them, of sulphur or an equivalent element in a suitable form.

The substitution of carefully prepared colloidal sols for such extracts largely avoids the risks of irregular and uncertain composition which inevitably accompany the use of such extracts.

Colloids in Veterinary Practice.

Colloidal silver and sulphur have yielded excellent results in veterinary practice, the former in the treatment of swellings, sprains, bruises, wounds, sores, rheumatism, thrush in the feet, fistula, various skin diseases and inflammation of the eyes, and the latter for cases where a deficiency of sulphur is indicated.

The Limitations of Colloids.

The selection and use of colloidal sols requires the same care and skill as the administration of any other remedies, but with the great advantage of being made specific and rational rather than empiric.

A word of warning may be expressed as to the use of unstable colloids in medicine. A number of colloidal preparations—particularly of silver and iodine—has been placed on the market which have not been properly stabilised. The use of these preparations has been accompanied by disappointing results, as it is essential (as previously mentioned) that the colloids exhibited should be stable in the presence of serum and saline solutions.

The failure of numerous colloidal sols of German (and some of British) origin created, in some minds, a prejudice against all colloidal remedies. The failures have been found, in every case examined, to have been wholly due to the method of preparation. Thus it has

have found that colloidal metals prepared by Bredig's method (dispersion by an electric arc with poles of the desired metal) are unsuitable for medicinal purposes, as they are not only unstable in themselves, but are rapidly decomposed by electrolytes present in the human organism. Where properly stabilised colloidal sols are employed they are as reliable as any of the preparations in the Pharmacopœia.

It should be observed that some so-called synthetic remedies are found to be colloidal sols, though this is not generally known. This has led to some curious misstatements in regard to the relative therapeutic values of colloids and synthetic drugs.

Owing to the impossibility of repressing all side reactions in making experiments on the living subject, pharmacology and chemotherapy are among the most inexact of sciences. Yet the success which has attended investigations on the use of colloids as remedial agents is so great as to call for the sympathetic interest of all who can appreciate what has been accomplished, and affords a basis of hope that further developments will be still more beneficial to suffering humanity. It is highly probable that serum and vaccine therapy will ultimately be resolved into questions of colloidal chemistry, but in the meantime the use of colloidal solutions of certain elements appears to offer a means whereby the various colloids can be accurately prepared and administered with a higher degree of efficiency than is possible with some of the more complex synthetic compounds at present in use.

The ever-increasing use of colloidal sols in military and private practice is a certain indication of their value, and among the indirect results of the World War, the facilities which it has given for the investigation of many hitherto obscure problems of disease and the opportunities which it has afforded for ascertaining the value and *rationale* of many new remedies, will be among the blessings of a catastrophe which is, otherwise, too awful to contemplate.

Literature.

The literature on the applications of colloid chemistry to biology and physiology,[30] and in the "Kolloidchemie Beihefte," "Kolloid Zeitschrift," and "Biochemische Zeitschrift" should be consulted.

Papers on the application of colloids in therapeutics also appear frequently in the "British Medical Journal," "The Practitioner," "The Lancet," and various foreign medical journals. Notwithstanding the voluminous literature on the general subject a vast amount of research into details remains unexplored. In the prosecution of further work, it is well to recall the words of a former president to the effect that "Medicine is no unworthy ally of the British Association and while her practice is ever more and more based on Science, the ceaseless efforts of her votaries are ever largely adding to the sum of abstract knowledge."[31]

[30] See "First Report on Colloidal Chemistry," British Association, 1917, pp. 85, 86. Also present Report, pp. 117–154.

[31] Sir J. Lister, "Interdependence of Science and the Healing Art." Presidential address to Brit. Assn., 1896.

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